

(NASA-CR-147904) HYPERGOLIC PROPELLANTS  
LIQUID AND VAPOR DISPOSAL, PHASE 4 Final  
Report (Florida Inst. of Tech.)

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HYPERGOLIC PROPELLANTS  
LIQUID AND VAPOR DISPOSAL

Phase 4 //

S Final Report //

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by

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## PREFACE

This study was conducted by Florida Institute of Technology under Contract NAS 10-8399, administered by the National Aeronautics and Space Administration, John F. Kennedy Space Center, Florida. The NASA Technical Representative for the contract was Mr. Harold H. Franks, DD-MDD. Florida Institute of Technology's study manager was Dr. Thomas E. Bowman, Professor of Mechanical Engineering. This report is the Final Report for Phase 4, a study of the disposal of contaminated aqueous solutions containing six specific organic substances.

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## CHAPTER I

### Introduction

Aerospace and ground support equipment require stringent cleaning processes to assure flight and personnel safety. Waste products resulting from the cleaning operations present a special disposal problem due to their generally toxic nature and their undesirable ecological impact. Common methods of disposal such as burning, dilution, ground dumping, or evaporation may be unacceptable in the future because of the potential requirement for more stringent pollution control.

Phase 4 of the study "Hypergolic Propellants - Liquid and Vapor Disposal" was concerned with the disposal of several of these waste products. Specifically, we studied the disposal of aqueous mixtures containing trichloroethylene, isopropyl alcohol (IPA), ethylene glycol, trichlorotrifluoroethane (Freon), methylethylketone (MEK), and methylene chloride. The greatest emphasis was on solutions of IPA containing monomethyl hydrazine (MMH), and of Freon containing oxides of nitrogen, because of the quantities of these wastes that will be generated during Space Shuttle operations.

Our general approach to this study was similar to that used in the first three phases, covering the disposal of the actual propellant wastes, although in Phase 4 we did not go into as much depth as in the earlier work. Basically, the work consisted of three sequential segments: a

survey of the current state of the art of disposal of these wastes, followed by a review and evaluation of the methods currently employed, followed by specific applications studies intended to define better disposal methods, or best approaches to existing methods, within the context of anticipated conditions and requirements at Kennedy Space Center.

The study was qualitatively somewhat different from our study of hypergolic propellant disposal in that all of the compounds of interest in this phase are common industrial chemicals, in widespread use throughout the country. Disposal problems are common to many industries, and disposal or recycling facilities for these chemicals have been established in many locations. As a result, one aspect of this phase was consideration of how Kennedy Space Center can best interface with existing collection and recycling operations, what the impact would be on these existing operations, and what influence future KSC operations might have on the need for additional regional collection networks and recycling centers. One problem that ordinary users do not encounter is the contamination of these waste solvents with highly toxic hypergolic propellants (especially monomethyl hydrazine), and this problem received special attention in our study.

The organization of this report does not follow the chronological sequence of tasks described above. For the sake of a more logical presentation, the State of the Art section is followed by the section dealing with Applications Studies, with the Evaluations and Recommendations section moved to the end of the main body of the report. As a part

of this Introduction, we have included subsections briefly describing the chemicals of interest and the important methods of disposal. The report does not treat, at any length, many of the general considerations that were detailed in the Final Report covering the first three phases, hereafter referred to as FR 1-3. For example, we do not as a general rule recommend or seriously consider any of the casual or uncontrolled disposal methods such as dumping on the ground, open burning, or open evaporation, for a number of reasons discussed in FR 1-3. Our avoidance of these methods does not imply that they are necessarily harmful in the case of unscheduled disposal of small quantities of waste product, but rather that they should not be considered in the case of any regularly occurring disposal situation, or for the disposal of significant quantities of any of these products.

Our general philosophy, as in the earlier portions of the study, is that environmental considerations are foremost. To a certain extent, these considerations are not limited to the local environment only. For example, the conservation of natural resources is an important part of any overall concern with the environment, and should be taken into account in considering the desirability of recycling a compound versus destroying it, perhaps especially so in the case of solvents manufactured from petroleum or those that could reasonably be used as fuels.



## MATERIAL DESCRIPTIONS

The paragraphs that follow present general descriptions of the basic physical characteristics and common applications of the six materials of interest. These descriptions were extracted from a variety of brochures and fact sheets supplied by the manufacturers. Specific data are presented farther on in this subsection.

### Isopropyl Alcohol

Isopropyl alcohol is a volatile, colorless, stable liquid with a characteristic alcoholic odor. It is similar to ethyl alcohol in solvent properties and evaporation rate. Isopropyl alcohol dissolves ethyl-cellulose, poly(vinyl butyral), alkaloids, shellac, some gums and natural resins, and many essential oils. Its high latent solvent power for cellulose nitrate and cellulose acetate butyrate, along with its moderate evaporation rate and its complete miscibility with most solvents, encourages isopropyl alcohol use in cellulose nitrate and cellulose acetate butyrate lacquers and thinners.

Isopropyl alcohol is used in the preparation of pharmaceuticals and cosmetics. Because of its bactericidal properties, it is used in liniments, rubbing compounds, and disinfectants. Isopropyl alcohol is used as a coupling agent in cleaners and polishes, an extractant, a dehydrating agent, a deicing fluid, a cooling medium in the frozen food industry, a gasoline additive, and a chemical intermediate.

### Trichlorotrifluoroethane

The "Freon" products are organic compounds containing one or more carbon atoms and fluorine. Chlorine, bromine and hydrogen atoms also may be present. Their principal characteristics include nonflammability, low toxicity, excellent thermal and chemical stability, high density coupled with low boiling point and low viscosity and surface tension.

Some of the "Freon" compounds have unique properties for use as solvents and cleaning agents. Of particular interest is "Freon" 113 (trichlorotrifluoroethane) and azeotropes of "Freon" 113 with other solvents such as alcohol, acetone, and methylene chloride. They are nonflammable, stable, low in toxicity, and exhibit a selective solvent action which permits their use for removing oil, grease, and dirt from many objects without harm to metal or plastic parts. The high density and low surface tension of the "Freon" solvents contribute to better soil removal. Their high stability and low boiling points permit easy recovery for reuse time after time.

These solvents have found wide application in vapor degreasing, spraying, flushing, ultrasonic cleaning, cold dipping, and combinations of the foregoing. As a result of their unique combination of physical properties, the "Freon" solvents are ideal for precision cleaning applications as well as a variety of industrial cleaning applications.

A "Freon" solvent drying system uses "Freon" solvents to quickly dry water-wet parts by displacing the water. It is an unusually low temperature drying system that eliminates many water spotting problems.

### Methyl Ethyl Ketone

Methyl ethyl ketone, MEK, a low boiling, fast evaporating solvent is a colorless, stable liquid, partially miscible with water. Methyl ethyl ketone first became available as a by-product of the wood distillation industry. Since commercial synthetic production began, many uses have been found.

Methyl ethyl ketone displays exceptionally good solvency for most resinous materials including EPON<sup>®</sup> resins, nitrocellulose, ethyl cellulose, cellulose acetate butyrate, acrylic resins, vinyl polymers and copolymers. Also readily dissolved are practically all synthetic and natural resins commonly employed in the formulation of printing inks, lacquers, and other types of coatings. In addition, its complete miscibility with most other solvents as well as alcohols and hydrocarbon diluents makes methyl ethyl ketone a highly desirable and versatile solvent in surface coating applications.

Although similar to acetone in solvency, methyl ethyl ketone has lower solubility in water, lower vapor pressure, and higher boiling point. These properties influence the selection of methyl ethyl ketone

as a replacement for acetone when factors other than economics and solvent power are important. A solvent for many of the film formers and resins used in the coatings industry, MEK is miscible with the usual cellulose nitrate lacquer solvents and diluents. Vinyl copolymers and acrylic lacquers often depend upon the solvent power of methyl ethyl ketone for their low viscosity and high diluent tolerance.

Other applications for methyl ethyl ketone include lubricating oil dewaxing, the preparation of solvent-dispersed adhesives and the manufacture of insecticides, artificial leather, industrial cleaning compounds, paint, lacquer and varnish removers, and printing inks used on cellulose derivatives. Methyl ethyl ketone also finds extensive use as an extracting agent and as a versatile chemical intermediate. A variety of syntheses from methyl ethyl ketone are possible using the carbonyl group as well as the adjacent hydrogen atoms on methyl ethyl ketone. Halogenation, oxidation, and condensation with aliphatic and aromatic compounds produce various intermediates useful in the manufacture of rubber accelerators and resins.

#### Trichloroethylene

Trichloroethylene historically has been the major solvent used in industrial vapor degreasing and cleaning applications. Where it is not limited by air pollution control restrictions, it is still frequently an excellent solvent choice because of its very aggressive solvent action on

oils, greases, waxes, tars, gums, rosins and on certain resins and polymers. It also has good stability and is economical to use. Its fast, efficient action leaves no residue or film to interfere with subsequent metal treatment such as welding, heat treating, electroplating or painting.

Trichloroethylene is heavier than water and immiscible with it. Like all chlorinated hydrocarbons, it is somewhat toxic. Although inhibited trichloroethylene has no flash or fire point, it is flammable within the range of 12-34 percent in air. The upper and lower limits vary slightly depending upon the temperature of the vapors at the time of the test.

By far the largest single use for trichloroethylene is in the degreasing of metals. Other uses include extraction of natural substances such as vegetable oils, waxes, animal fats, and botanicals; in drycleaning; a flame-proof solvent for adhesives; a dehydrating agent for alcohol; in medicine as an anesthetic; and as an organic intermediate.

Trichloroethylene, among all the chlorinated solvents, has been singled out in some areas of the country for atmospheric emissions control.

#### Methylene Chloride

Methylene chloride is a clear, colorless liquid which has no flash or fire point. It is one of the least toxic of the chlorinated hydrocarbons,

but like all of these compounds is somewhat toxic. Methylene chloride is quite stable and can be used in the presence of air, light, and moisture. However, excessive moisture at elevated temperatures may cause hydrolysis.

Its principal use is in the manufacture of nonflammable paint and varnish removers. It is also used as an additive to petroleum solvents to raise the flash point, low-temperature heat transfer medium, intermediate in chemical processes, and as an extraction agent for some substances which are unstable at the higher boiling points of other solvents. Other uses include as a plastic-stripping compound, a fire suppressant for flammable solvents, a refrigerant, a vapor-pressure-depressant in aerosol formulations, and a carrier solvent for plastic-based adhesives.

The use of methylene chloride for special vapor degreasing applications has been known for many years. Most recently its acceptance has been boosted by the need for additional alternate solvents to replace trichloroethylene in those areas around the country where the "Rule 66-type" regulations have been put into effect. Methylene chloride is a very versatile solvent, aggressive towards many oils, fats, greases, waxes, tars, plastics, resins, polymers, lacquers and both synthetic and natural rubber. Its use is considered particularly where parts might be damaged by the higher boiling temperatures of the other chlorinated degreasing solvents or where its aggressive solvency powers are specifically required. In this latter connection, it should be taken into account that some plastics

and elastomers normally used in chlorinated solvents service—for hose, gaskets, containers, etc.—will undergo degradation when continuously in contact with methylene chloride.

This solvent will dissolve more water than any of the other chlorinateds. Then, during long periods of contact with water at the boiling point, methylene chloride will slowly hydrolyze to produce hydrochloric acid and other by-products.

Methylene chloride has no flash point or fire point by standard test methods, and is classed as nonflammable and nonexplosive at ordinary temperatures. However, its vapors can become moderately flammable at elevated temperatures or when subjected to an intensive source of ignition such as an electric arc.

### Ethylene Glycol

First prepared by Wurtz in 1859, ethylene glycol remained a laboratory curiosity until 1904. At that time a German patent was issued covering the use of ethylene glycol dinitrate as an antifreeze additive in the manufacture of nitroglycerine. But ethylene glycol was not available in commercial quantities until the early 1920's and it was another fifteen years before its use as an automotive antifreeze was recognized. Today, annual production rate of ethylene glycol is over two billion pounds.

Ethylene glycol is a clear, water-white, slightly viscous, nearly odorless, non-corrosive, hygroscopic liquid. It is completely miscible

with water, alcohols, ketones and partially miscible with hydrocarbons and linseed oil. With excellent heat transfer properties, ethylene glycol also has a low vapor pressure and a boiling point more than 100°C higher than that of ethyl alcohol.

Ethylene glycol has many and varied uses; the most important of which is its use in all-weather automobile cooling systems. The low volatility and non-solvent action on automobile finishes of ethylene glycol, coupled with its ability to lower the freezing point of water without appreciably reducing its cooling effect, make it the principal component of antifreeze formulations for use in automobile radiators. The antifreeze ability of ethylene glycol is also put to use in de-icing solutions for automobile windshields and aircraft, in formulation of latex paints, and in fire extinguishers and sprinkler systems. It is used as a high and low temperature coolant, and in hydrolubes where it also acts as a diluent and coupler.

The use of ethylene glycol in brake, shock absorber, and other hydraulic fluids helps counteract rubber swelling. It also dissolves inhibitors and prevents foam formation.

Ethylene glycol is nitrated to prepare ethylene glycol dinitrate, a freezing point depressant used in the manufacture of low-freezing dynamite.

Another important end use for ethylene glycol is the manufacture of polyester resins for laminating and casting. Ethylene glycol is



reacted with maleic or phthalic anhydride and vinyl type monomers to produce laminating resins used in making furniture, suitcases, automobile bodies, and boat hulls. It also reacts with phthalic anhydride to form alkyd resins used in surface coatings. Other reaction products are polyester fibers and films from ethylene glycol and dimethyl terephthalate or terephthalic acid, and rosin esters for use as plasticizers.

Ethylene glycol is also used as a non-volatile solvent and suspension medium in electrolytic capacitors because it does not attack aluminum and because it has excellent electrical properties.

The excellent humectant properties of ethylene glycol are utilized in treating textile fibers, paper, adhesives, printing inks, leather, glue, and cellophane. The pliability, durability and softness of these products are enhanced by the hygroscopicity of ethylene glycol.

Table I, at the end of this subsection, presents a number of the important properties of the six chemical compounds of interest. Most of this information was extracted from "Technical Assistance Data System" computerized printouts provided by the Environmental Protection Agency. This information source also includes data on transportation modes, production sites, effects on water treatment processes, and many other topics not included in this table. Air pollution characteristics are rated as "slight" for IPA, MEK, and ethylene glycol, while trichloroethylene is rated as "toxic."

Other data in Table I are taken from TRW Report No. 21485-6013-RU-00<sup>1</sup>. This report is the result of a very extensive study of disposal techniques for hazardous waste products of all types, and has been a source that has been most helpful to us in both Phases 1 and 4 of our study.

In general, trichloroethylene seems to be regarded by the EPA as the most hazardous of the materials: "Highly toxic when inhaled. Moderately toxic by all other routes. Can be absorbed through skin. Dissolves (in water) very very slowly. Affects central nervous system. May cause dermatitis or eye irritation. Can suppress kidney action if taken orally. Symptoms include tachycardia, sialorrhea, nausea, vomiting, headache, confusion, convulsions. Overdoses can cause psychosis and acute yellow atrophy of liver. Narcotic at high concentrations. Dermatitis, facial nerve paralysis or irregular heart functioning may result from repeated subacute exposure levels." It should be mentioned, for the sake of proper perspective, that this chemical is readily available to the public as a dry cleaning fluid,

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<sup>1</sup> R. S. Ottinger, J. L. Blumenthal, D. F. Dal Porto, G. I. Gruber, M. J. Santy, and C. C. Shih, "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste," Report No. 21485-6013-RU-00, TRW Systems Group, 1 February 1973, prepared for Environmental Protection Agency, Contract No. 38-03-0089.

especially since the removal of carbon tetrachloride from the general marketplace.

The hazards associated with isopropyl alcohol are described in the EPA's Technical Assistance Data System (TADS) as follows:

"Inhalation causes headache, nausea, dizziness, mental depression, vomiting, coma, and death. Can cause corneal burns and eye damage. Mild irritation at 400 ppm provides good warning property."

Methyl ethyl ketone's hazards: "Moderately toxic via inhalation. Irritation offers a good warning before damage occurs. TLV 20 ppm. High concentrations—headache, nausea, narcosis."

Ethylene glycol: "Ingestive poison. Transient stimulation of central nervous system followed by depression, vomiting, drowsiness, coma, respiratory failure, convulsions, renal damage, and death. Slight ingestive and irritant hazard with chronic exposure."

Within the context of this study, ingestive hazards are of concern in connection with any discharge to a stream or aquifer, and inhalation hazards are of concern in connection with any atmospheric discharge.

TABLE I

Solvent	Synonyms	Chemical Formula
Ethylene Glycol	1,2-Ethanediol Glycol Alcohol	$\text{HOCH}_2\text{CH}_2\text{OH}$
Trichloro-trifluoro-ethane	Freon 113 <sup>®</sup>	$\text{CCl}_3\text{CF}_3$
Isopropyl Alcohol	Isopropanol 2-propanol Secondary-propyl-alcohol Petrohol Dimethylcarbinol IPA	$\text{CH}_3\text{CHOHCH}_3$
Methylene Chloride	Dichloromethane	$\text{CH}_2\text{Cl}_2$
Methyl Ethyl Ketone	Ethyl Methyl Ketone 2-Butanone MEK	$\text{CH}_3\text{COCH}_2\text{CH}_3$
Trichloro-ethylene	Trichloroethane Tri-clene Trilene Ethynyl Trichloride etc.	$\text{CHClCCl}_2$

TABLE I (Continued)

Solvent	Mol. Wt.	Boiling Point @ 1 atm.	Freezing Point
Ethylene Glycol	62.1	197.5C 387F	-12.60C 9.6F
Trichloro- trifluoro- ethane	187.39	47.6C 117F	-35C -31F
Isopropyl Alcohol	60.09	82.3C 180F	-85.9C -129F
Methylene Chloride	84.94	40.1C 104F	-96.7C -142F
Methyl Ethyl Ketone	72.1	79.57C 176F	-85.9C -121F
Trichloro- ethylene	131.4	86.9C 188F	-86.8C -125F

TABLE I (Continued)

Solvent	Liquid Specific Gravity, referred to water	Vapor Pressure
Ethylene Glycol	1.113 @ 25/25C	.05 mm @ 20°C
Trichloro-trifluoro-ethane	1.5702 @ 4/4C	6.5 psig @ 77°F
Isopropyl Alcohol	.7854 @ 20/4C	33 mm @ 20°C or .6 psig @ 68°F
Methylene Chloride	1.326 @ 20/4C	380 mm @ 22°C
Methyl Ethyl Ketone	.80615 @ 20/20C	71.2 mm @ 20°C
Trichloro-ethylene	1.4556 @ 25/4C	40 mm @ 11.9°C or 1.16 psig @ 70°C

TABLE I (Continued)

Solvent	Liquid Specific Gravity, referred to air, at STP	Solubility (ppm)
Ethylene Glycol	2.14	1,000,000 @ 25°C
Trichloro-trifluoro-ethane	6.47	
Isopropyl Alcohol	2.07	1,000,000 @ 25°C
Methylene Chloride	2.93	
Methyl Ethyl Ketone	2.41	100,000 @ 25°C
Trichloro-ethylene	4.53	160 @ 25°C

TABLE I (Continued)

Solvent	Flash Point		Autoignition Temperature	
	°C	°F	°C	°F
Ethylene Glycol	111	232 (cc)	413	775
Trichlorotrifluoroethane	Non-flamable	Non-flamable	650	1200
Isopropyl Alcohol	21.1 (oc) 11.7 (cc)	70 (coc)	399	750
Methylene Chloride	Prac. non-flamable	Prac. non-flamable	662	1224
Methyl Ethyl Ketone	-5.6 (toc)	22	516	960
Trichloroethylene	32.1	90	419	786



TABLE I (Continued)

Solvent	Fire Hazard
Ethylene Glycol	Slight when exposed to heat or flame. Can react with oxidizing materials.
Trichloro-trifluoroethane	Very slight when exposed to heat or flame.
Isopropyl Alcohol	Dangerous when exposed to heat or flame.
Methylene Chloride	None.
Methyl Ethyl Ketone	Danerous when exposed to heat or flame. Can react with oxidizing material.
Trichloro-ethylene	Slight when exposed to heat or flame. High concentration of trichloroethylene vapor in high temperature air can burn mildly if plied with a strong flame. Although such a condition is difficult to produce, flames or arcs should not be used in closed equipment which contains any solvent residue or vapor.

TABLE I (Continued)

Solvent	Explosive Hazard	Explosive Limits
Ethylene Glycol	Moderate when exposed to flame.	3.2% (L. E. L.)
Trichlorotrifluoroethane	Dangerous when heated to decomposition. May emit highly toxic fumes of fluorine and chlorine.	
Isopropyl Alcohol		(2.5-5.2%)
Methylene Chloride	None, under ordinary conditions but will form explosive mixture in atmospheres having high oxygen content.	15.5-66.4% in Oxygen
Methyl Ethyl Ketone	Moderate when exposed to flame.	1.81-11.5%
Trichloroethylene		

TABLE I (Continued)

Solvent	Toxic Hazard Rating	U. S. Occupational Standard Time Weighted Average (USOSTWA) *
Ethylene Glycol	Acute Local: irritant 1 Acute Systemic: ingestion 3 (Lethal dose for man reported to be 100 ml) Chronic Local: irritant 1 Chronic Systemic: ingestion	
Trichlorotrifluoroethane	Acute Local: U Acute Systemic: Inhalation 1 Chronic Local: U Chronic Systemic: U	
Isopropyl Alcohol	Acute Local: irritant 1, ingestion 1, inhalation 1 Acute Systemic: ingestion 2 Chronic Local: inhalation 2 Chronic Systemic: ingestion 1, inhalation 1	400 ppm in air 1020 mg per m <sup>3</sup> air
Methylene Chloride	Acute Local: irritant 2, ingestion 2, inhalation 2 Acute Systemic: ingestion 2, inhalation 3, skin absorption 2 Chronic Local: U	500 ppm in air 1740 mg per cubic meter air
Methyl Ethyl Ketone	Acute Local: irritant 1, ingestion 1, inhalation 1 Acute Systemic: inhalation 2 Chronic Local: irritant 1 Chronic Systemic: U	200 ppm in air 588 mg per m <sup>3</sup> air
Trichloroethylene	Acute Local: irritant 1, ingestion 1, inhalation 1 Acute Systemic: ingestion 2, inhalation 2, skin absorption 2 Chronic Local: irritant 1 Chronic Systemic: U	100 ppm air 536 mg per m <sup>3</sup> air

## Toxic Rating Code

- 0 = None  
1 = Slight  
2 = Moderate  
3 = High  
U = Unknown

\* The Toxic Substances List,  
1974 Edition, Published by  
U. S. D. H. E. W., P. H. S., C. D. C.,  
N. I. O. S. H., Rockville, Md.  
20852, June 1974.

## Process Descriptions

A number of processes can be conceived for disposal of the six chemicals of interest. For the purpose of general descriptions, these processes may be categorized as belonging to three general types:

- (1) Thermal processes: combustion or thermal decomposition, with or without stack gas scrubbing.
- (2) Distillation processes for solvent recovery.
- (3) Chemical and biological processes: aeration ponds or lagoons, oxidation ditches, stabilization ponds, treatment tanks, or catalytic decomposition.

The first category normally involves a controlled incinerator, in which a fuel-air mixture is burned. The waste product is added to the combustion zone and either takes part in the combustion process, or is thermally decomposed. Detailed general descriptions and discussion were presented in FR 1-3. Scrubbing of the products of combustion is indicated in the case of the chlorinated hydrocarbons to reduce halogen emissions.

The second category includes both simple distillation and rectification:

Distillation is the separation of the constituents of a liquid mixture by partial vaporization of the mixture and separate recovery

of vapor and residue. The completeness of separation depends upon the boiling points of the components involved and the efficiency of the distillation process.

Rectification is a more complex distillation carried out in such a way that the vapor rising from a still comes in contact with a condensed portion of vapor previously evolved from the same still. A transfer of material and an interchange of heat result from the contact, thereby securing a greater enrichment of the vapor in the more volatile components than could be secured with a single distillation operation using the same amount of heat. Separation of mixtures of homologs or materials with relatively close boiling points is possible. Rectification equipment is generally more elaborate than that for simple batch distillation.

In the third category, our primary interest in this study is in the biological and chemical changes that take place in various types of ponds. The paragraphs that follow present general descriptions and background information on three common types of pond used for bio-treating numerous organic wastes generated by public and industrial establishments. Under suitable conditions, ponds are useful and economical units for the treatment of industrial wastes. They are particularly effective in

areas where land is available and sunshine sufficient to provide the photosynthesis important to their successful functioning.

### Stabilization Ponds

A stabilization pond utilizes bacteria to stabilize organic substances. In aerobic stabilization ponds, the dissolved degradable wastes are stabilized by aerobic microbic organisms supplied with needed oxygen by algal photosyntheses as well as by gas transfer at the pond surface (generally without artificial means). In anaerobic ponds the degradable substances are stabilized by anaerobic microbic organisms in the continuous absence of dissolved oxygen. In hetero-aerobic ponds, the degradable wastes are stabilized by facultative aerobic and anaerobic organisms because of cyclic changes from aerobic to anaerobic conditions at different pond levels.

Design procedures\* for stabilization ponds are imprecise.

Rate-determining factors are:

- (1) Detention time, ordinarily measured in days. General design values are 15 to 30 days.
- (2) Pond depth. General design values are 3-4 ft. for aerobic ponds, 6-10 ft. for anaerobic ponds.

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\* Herman, E. R. and Gloyna, E. F., Waste Stabilization Ponds III, Formulation of Design Equations, J. Water Pollution Control Fed., 30, 963 (1958).

- (3) Pond loading, expressed in pounds of BOD<sub>5</sub> at 20° C.
- (4) Pond temperature.
- (5) Visible light energy reaching the water surface.
- (6) Efficiency of conversion of light energy into chemical energy — usually 2 - 6 %. Efficiency is also dependent on the quality and concentration of nutrients, degree of mixing, detention period and other factors.

The essential components of the stabilization process are:

- (1) Seeding with proper microorganisms.
- (2) Creation of biological floc for the utilization of the organic solvents for cell growth.
- (3) Liberation of relatively stable, innocuous end products such as CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>.
- (4) Provision of sufficient oxygen.
- (5) Possible disposal of excess sludge.

If desired, outlet structures can permit changes in depth, withdrawal of effluent from below the water surface, and complete drainage of the pond. Central inlets are normally provided for ponds that lose most of their water by evaporation or seepage. The top of the dike should be sufficiently wide to accommodate maintenance vehicles and fenced to keep out animals. Emergent vegetation should be destroyed and mosquito breeding not tolerated. A major disadvantage of a stabilization pond is the long detention time.

### Aerated Ponds or Lagoons

An aerated pond is defined as a basin in which dissolved or suspended degradable substances, such as solvent wastes, are stabilized by facultative and/or aerobic microorganisms, supplied with the required dissolved oxygen by algal photosynthesis and gas transfer at the pond surface, with support by mechanical or diffused aeration equipment. Depth is usually 6-17 feet.

In the aerobic pond sufficient air is introduced to enhance suspension of solids by eddies near the bottom of the pond to minimize sludge deposition. Since isopropanol, methyl ethyl ketone, and ethylene glycol, as well as the hypergolic fuels and oxidizers, are readily soluble in water, the sludging problem is limited to suspension of the biological cells rather than their food supply.

In the facultative pond, only enough air is introduced to maintain turbulence levels, to insure distribution of oxygen through the pond with some settling of sludge. This sludge may undergo anaerobic decomposition. Facultative ponds utilize aerobic biochemical oxidation on the upper pond level and anaerobic decomposition in the lower or bottom level.

Mechanical aeration creates a certain amount of turbulence to maintain the floc in suspension and keep the water circulated. The effluent may be periodically withdrawn by pumping; alternately, a



variable level may be maintained by natural evaporation, seepage and precipitation. A slow benthal sludge buildup can be expected over an extended period of time. Excess sludge can be dried on sand beds or disposed of in a sanitary landfill every few years.

Aerated ponds are used successfully to provide high degrees of water treatment with low overall system cost, including initial, operating and maintenance costs. Further, the oxygen transfer and mixing efficiencies are high. Consistent year-round treatment is possible with a minimum of operator attention.

#### Oxidation Ditch

An oxidation ditch is a form of stabilization unit specifically designed to treat liquid organic wastes by biological, chemical, and physical processes somewhat similar to natural purification but at an enhanced rate.

The oxidation ditch utilizes bacteria to aerobically stabilize the organic materials and nutrients present in the waste water, resulting in the oxidation of C to  $\text{CO}_2$ ,  $\text{H}_2$  to  $\text{H}_2\text{O}$ , and reduction of  $\text{N}_2$  to  $\text{NH}_3$ . The  $\text{O}_2$  for the bacteria is supplied by both air surface transfer and the metabolism of algae in the pond. The cycle is completed when the algae use the waste stabilization products  $\text{CO}_2$  and  $\text{NH}_3$  to synthesize new cells in the presence of sunlight, and thereby liberate  $\text{O}_2$  as an end product to be used

by the bacteria for oxidizing the organic wastes and synthesizing bacterial protoplasm.

The simplest oxidation ditch is a mechanically aerated continuous channel. A displacement velocity of about 1 ft. per second keeps the floc in suspension. The rotor runs across the channel. Depths are 3-5 ft. and detention period from 1 to 3 days. Effluent is not withdrawn until the depth of water reaches the highest operating level. The influent is then cut off and the rotor stopped. The sludge is allowed to settle. Excess sludge is withdrawn through bottom outlets to drying beds or other disposal. The clarified supernatant, if it meets environmental requirements, can be disposed of into a stream or reused. The operating routine is then repeated. Continuous operation can be performed with addition of an effluent settling tank for excess sludge removal.

In practice, the oxidation ditch is an economical means of treatment since it does not require extensive accessory equipment common to other methods of treating wastes. For example, primary settling and sludge digestion units are usually not employed. The system consists of a ditch, a final clarifier and dewatering means for the small amount of sludge that is withdrawn periodically from the system. The principal advantages of the oxidation ditch are:

- (1) extreme simplicity of operation
- (2) low construction and operating costs
- (3) easy maintenance
- (4) flexibility in the degree of treatment

Many industrial wastes have been treated satisfactorily in oxidation ditches including oil refinery, fruit canning, slaughterhouse, and other wastes. BOD loadings up to 5000 to 8000 mg/l have been treated with BOD removal up to 80-95%.

## CHAPTER II

### State of the Art

#### A. RECOMMENDATIONS FROM OTHER SOURCES

Our first step in assessing the "current state of the art" was to ascertain what regulations, if any, currently exist regarding the disposal of the materials of interest. The conclusion was that nothing specific to these materials does exist, other than the established Threshold Limit Values and Maximum Acceptable Concentrations quoted below in the subsection on the TRW Report. In the absence of specific regulations, our next step was to collect information on recommendations for waste disposal resulting from earlier studies. Most valuable in this regard was TRW Report No. 21485-6013-RU-00, which was referred to in the Introduction and also extensively referred to in FR 1-3. These recommendations are listed below, along with short recommendations extracted from the Environmental Protection Agency's "Technical Assistance Data System."

## Ethylene Glycol and Isopropyl Alcohol

The following statements are extracted from the TRW Report,  
Volume 10, page 121:

"Manufacturers that use alcohols as chemical intermediates or process solvents recycle as much material as possible. In addition, a certain amount of contaminated alcohols are eligible for reprocessing. This is the method of choice wherever possible.

"The alcohols treated in this report not only have a low level of toxicity but they can be biodegraded very rapidly by unacclimated activated sludges. This is due in part to the fact that most are either naturally occurring or components present in normal sewage. Thus, the best method of disposal is via municipal sewage treatment plants, provided the rate of discharge is uniform.

"Bulk quantities of contaminated alcohols that can not be reprocessed or released by controlled dilution can best be disposed of by incineration. Since this will probably be an unusual occurrence, this is best done at municipal or industrial incineration sites."

The TRW Report also quotes established Threshold Limit Values (TLV) and Maximum Allowable Concentrations (MAC) for these materials, as follows:

Ethylene Glycol: MAC = 200 ppm

(no TLV listed)

Isopropyl Alcohol: TLV = 400 ppm (980 mg/M<sup>3</sup>)

MAC = 400 ppm

Provisional Limits recommended by this same report are as follows:

Ethylene Glycol: 2.0 mg/M<sup>3</sup> in air

1.0 ppm in water and soil

Isopropyl Alcohol: 4.0 ppm (9.8 mg/M<sup>3</sup>) in air

49 ppm in water and soil

The Technical Assistance Data System recommendation for disposal of both of these materials is:

"Spray into incinerator or burn in paper packaging.

Additional flammable solvent may be added."

#### Aliphatic Halogenated Hydrocarbons

This category includes methylene chloride, trichloroethylene, and trichlorotrifluoroethane, as well as a wide variety

of other similar materials, including other Freon® fluorochloro-hydrocarbons.

The following statements are extracted from the TRW Report, Volume 10, pages 292-293:

"The dry cleaning, refrigeration, degreasing and solvent extraction industries, as well as processors using halocarbons as raw materials, all recycle as much of their halocarbons as possible. For small users or companies with badly contaminated lots, commercial solvent reclaimers reprocess the materials for further use.

"Badly contaminated solvents that cannot be reclaimed, as well as chlorinated and non-chlorinated residues and sludges, can be disposed of by incineration. Some of the materials, especially those with high chlorine content may not support combustion by themselves, but can be burned if an auxiliary fuel is used. Care must be exercised to assure complete combustion. An acid scrubber is necessary to remove the halo acids produced. In this manner, both long- and short-term environment effects are eliminated at the sources in one simple disposal step.

"Deposit by landfill of halogen-containing waste . . . . . presents a serious long-term environmental hazard to man, animals and fish. These materials are toxic and to some extent water soluble. Biodegradation will further increase their mobility. Thus, landfill disposal of these wastes represents an excessive, long-term threat to underground water supplies and must be considered much less acceptable than Option No. 2 (incineration). Option No. 3 is acceptable only when the landfill site is totally isolated from ground and surface water and meets California Class 1 standards."

The Technical Assistance Data System recommendation for disposal of trichloroethylene is: "Can be poured on dry sand and allowed to vaporize in isolated locations. Purify by distillation or return to supplier."

The TRW Report quotes established Threshold Limit Values (TLV) and Maximum Allowable Concentrations (MAC) for some of these materials:

Methylene Chloride:	TLV	=	500 ppm (1740 mg/M <sup>3</sup> )
	MAC	=	500 ppm
Trichloroethylene:	TLV	=	100 ppm (535 mg/M <sup>3</sup> )
	MAC	=	100 ppm

The same report recommends Provisional Limits for these materials as follows:



Methylene Chloride: 5 ppm (17.4 mg/M<sup>3</sup>) in air

87 ppm in water and soil

Trichloroethylene: 1.0 ppm (5.35 mg/M<sup>3</sup>) in air

26.75 ppm in water and soil

The proprietary solvent/refrigerant trichlorotrifluoroethane (Freon 113<sup>®</sup>) is not explicitly listed in the TRW Report. However, three closely related compounds are listed: dichlorofluoromethane (Freon 12<sup>®</sup>), dichlorotetrafluoroethane (Freon 114<sup>®</sup>) and trichlorofluoromethane. In all three cases, the established TLV's and MAC's are 1000 ppm, and TRW's recommended Provisional Limits in air are 10 ppm. The recommended Provisional Limits in water and soil are 247.5, 350, and 280 ppm, respectively, for these three compounds. It should be mentioned that at the time of the present report, the question of atmospheric release of halogenated hydrocarbons, and especially the very stable Freon<sup>®</sup> compounds, is the subject of a rather massive national investigation. It seems almost certain that new standards and regulations will be forthcoming within the next two years. Although the primary problem is one of overall quantities rather than source-point concentrations, it is certainly possible that new MAC values will be promulgated as a part of any new system of controls, and this possibility must be factored into any facilities planning that might involve release of Freon<sup>®</sup> vapors.

### Methyl Ethyl Ketone

The following statements are extracted from the section of the TRW Report dealing with aldehydes and ketones (Volume 10, page 5):

"Manufacturers that use these materials as chemical intermediates or process solvents recycle as much material as possible. In addition, a certain amount of contaminated material may be reprocessed. This is the method of choice wherever possible.

"Aldehydes and ketones treated in this report not only have a low level of toxicity but they can be biodegraded very rapidly by unacclimated activated sludges. This is due in part to the fact that they can, in most cases, be simply oxidized by chemical or biological means to acids that are the same or very similar to carboxylic acids present in normal sewage.

"Thus, an acceptable method of disposal is via municipal sewage treatment plants, provided the rate of discharge is uniform.

"Bulk quantities of contaminated aliphatic aldehydes and ketones that can not be reprocessed or released by controlled dilution can best be disposed of by incineration. This is the

method of choice where adequate biological treatment facilities are not available. "

The Technical Assistance Data System recommendation is:

"Dilute solutions can be discharged directly into sewage treatment facilities. Spray into incinerator or burn in paper packaging.

Additional flammable solvent may be added. "

The TRW Report quotes the established Threshold Limit Value as 200 ppm (590 mg/M<sup>3</sup>), and the Maximum Allowable Concentration as 250 ppm. The same report recommends Provisional Limits of 2 ppm (5.9 mg/M<sup>3</sup>) in air and 29.5 ppm in water and soil.

## B. SURVEY OF CHEMICAL MANUFACTURERS

The next step after seeking out disposal recommendations that have resulted from other studies was to contact the manufacturers of the chemicals in question to ask for their recommendations. Twenty-eight chemical companies were contacted, and replies were received from twenty of them. All of them referred to either Material Safety Data Sheets based on OSHA Form 20, or to Manufacturing Chemists Association Chemical Safety Data Sheets. The OSHA forms do not refer specifically to disposal; the Manufacturing Chemists Association pamphlets do, but are generally rather vague. Their recommendations are quoted at the end of this section.

Specific information supplied by some of the chemical companies in their letters of reply included the following:

Jefferson Chemical Company, Austin, Texas: "The only disposal technique we recommend (for ethylene glycol) is incineration. Although ethylene glycol is biodegradable, the rate of biodegradation would vary with the bacterial strains in the test. We know of no published standards for disposal of ethylene glycol and no reclamation centers in the State of Florida."

Vulcan Materials Company, Wichita, Kansas: "The only approved disposal method for methylene chloride is incineration in a chemical furnace with an appropriate scrubbing system for

removal of the acid gas produced. I do not know of any reclamation centers in the State of Florida. "

PPG Industries, Pittsburgh, Pennsylvania: "Following contamination in use, chlorinated solvents are normally purified by distillation. Purification occurs both in centralized reclamation centers and on a smaller scale at the actual solvent use site. PPG Industries is indirectly involved in this aspect serving only as technical advisors. The volatility of the contaminants is usually significantly different from that of the solvent so that simple rather than rectification type distillation is required. Stills usually operate at atmospheric pressure, although partial vacuums are sometimes used. Relatively pure solvent vapors are removed as feed is introduced. The condensed vapors may then be recycled to its original use. Steam distillation can also be used .... Chlorinated solvents can be disposed of by thermal decomposition. At temperatures above 1300°F, the solvent molecules break down and form HCl and CO<sub>2</sub>. In these operations, the acid is usually neutralized before discharge. Incineration is used by some reclaimers to dispose of distillation residues. There are two reclamation centers in Florida — Gold Coast Oil in Miami and Ernie Supply Company in Tampa. "

ARCO Chemical Company, Channelview, Texas: "On occasion we alternately dispose of minor quantities of these materials (IPA

and MEK). I have listed below the various methods by which we alternately handle streams of the two solvents in question.

(1) Off-test and/or by-product streams of these materials are accumulated in on-site tankage, are reprocessed in the appropriate operating units and are thereby recovered for sale.

(2) Waste streams of these materials are accumulated in on-site tankage and utilized as an auxiliary boiler fuel source.

(3) Concentrated aqueous waste streams not suitable for boiler fuel are eliminated by sub-surface injection into a federally and state approved waste disposal well.

(4) Dilute aqueous waste streams (parts per million range) are eliminated by treatment in our biological facilities.

(5) If any waste stream cannot be processed by any of the above methods, contractual arrangements are made with local industrial waste haulers to remove the waste stream from our property for a fee.

"I do not have knowledge of any reclamation centers in the State of Florida."

Exxon Chemical Company, Houston, Texas: "We would recommend the same disposal procedures (as given in Chemical Safety Data Sheet SD-98 for Isopropyl Alcohol) for methyl ethyl ketone."

Stauffer Chemical Company, Houston, Texas: "The normal and best method for disposal of any quantity of methylene chloride is through a spent solvent reclaimer. We are not familiar with reclaimers in Florida."

Allied Chemical, Morristown, New Jersey: "Disposal of methylene chloride in quantity is generally effected by materials scavengers who, depending on market conditions, pay or are paid to remove and reclaim methylene chloride. This frequently includes redistillation. We do not have familiarity with reclaimers in Florida."

BASF Wyandotte Corporation, Wyandotte, Michigan: "The only fully acceptable method of disposing of ethylene glycol is incineration. Small quantities could be buried in the ground or washed to the sewer. Ethylene glycol will eventually become biodegraded since it is 100% organic."

Olin Chemicals, Stamford, Connecticut: "The safest way to dispose of ethylene glycol is by incineration. Spills may be absorbed onto a burnable absorbent material and incinerated. The products of combustion are carbon dioxide and water. In the event of insufficient oxygen some carbon monoxide will be formed. Small spills .... are usually washed away with large amounts of

water. The ethylene glycol molecule is bio-degradable with time. "

Hooker Electrochemical, Niagara Falls, New York:

"Recommended disposal of these materials (methylene chloride and trichloroethylene) are to incinerate in equipment designed to handle HCl, contract services for reclaiming or disposal, or pouring on dry sand, earth, or ashes at a safe distance from occupied areas and allowing to evaporate into the atmosphere according to local pollution control. Trichloroethylene is repeatedly distilled and reused. The greatest loss is due to evaporation to the atmosphere during use. There usually are only small concentrations in the residues which can be incinerated or allowed to evaporate as discussed above. "

E. I. du Pont de Nemours and Company, Wilmington, Delaware: "Where practical, recovery of (Freon <sup>®</sup>) solvents is recommended and economically desirable. Residual heels from such recovery would normally be disposed of by burying. Currently, recovery of the more volatile products is not practiced. It should be noted that original specifications for fluorocarbon solvents are strict, and extreme caution is required when approving recovered solvent for precision use. "



Shell Chemical Company, Houston, Texas: "The disposal technique (for ethylene glycol, isopropyl alcohol, and methyl ethyl ketone) are relatively simple unless they are badly contaminated with complicating extraneous materials. Reclamation, incineration, and biotreating are the three main techniques applied and are preferred in that order for obvious reasons. Reclamation is undoubtedly more feasible for the manufacturers than it would be for most users, because of the availability of facilities for purification and recycle. Presuming therefore that any reclaiming would be done for the Space Center by an outside facility, we will discuss below only incineration and biotreating of these materials.

#### "Incineration

"The heat of combustion is about the same for any of the three materials and is only about 25 percent less than for an equal volume of fuel oil. No combustion problems nor any unusual combustion products are encountered. Public interest is therefore best served if any substantial amounts of these materials which cannot be reclaimed are used to fire furnaces or other heat recovering equipment. Contamination with materials containing nitrogen, sulfur, or the halogens, or the presence of heavy metals introduces

complications, as does the presence of substantial amounts of water.

"All of the materials are water soluble and can pick up large amounts of water in use or in storage. At 50 percent water the heating value declines to about one third of that of fuel oil. At still higher dilutions the amount of useful heat recovered becomes too small to be attractive, and may actually become negative because of the heat required to vaporize the large quantities of water. Even here this type of incineration is still a viable disposal method, and the extra fuel required may prove to be less of a burden on public resources than the other feasible disposal techniques.

#### "Biotreating

"Where these solvents are contaminated with very large amounts of water, disposal via some type of biological treatment is recommended. All three are readily biodegraded. No special precautions are required unless they are significantly contaminated and if the volumes are within the available capacity of the local municipal sewage treatment facility, the Space Center would be wise to consider this avenue. Many local sewage treatment authorities are interested in contract treatment arrangements with industry. These three materials are within the ability of such a treatment plant, if the load is

not so large as to overwhelm the normal, sewage orientation of the facility and the operating staff, and if the necessary capacity can be made available. Small quantities of concentrated solvent may also be most logically handled via this route.

"Our inquiries in your behalf have not revealed the existence of any company offering a reclamation service in Florida."

This list of quotations does not include excerpts from the responses of all of the chemical companies that replied, as many were noncommittal or simply referenced the Safety Data Sheets quoted below. In addition, some of them did refer us to solvent reclaimers in Florida, and these reclaimers are the subject of a separate subsection of this report.

The following quotations are from the Waste Disposal sections of the Chemical Safety Data Sheets published by the Manufacturing Chemists' Association, Inc.

Sheet SD-14, Trichloroethylene:

"Waste disposal of trichloroethylene depends to a great extent upon local conditions. Be sure that all Federal, State and local regulations regarding health and pollution are followed. The supplier will be able to furnish good advice on this matter."

"Residue may be poured on dry sand, earth, or ashes at a safe distance from occupied areas and allowed to evaporate into the atmosphere."

Sheet SD-86, Methylene Chloride:

"Residue may be poured on dry sand, earth or ashes at a safe distance from occupied areas and allowed to evaporate into the atmosphere."

Sheet SD-98, Isopropyl Alcohol:

"All local, state and federal regulations concerning waste disposal to streams, municipal treatment plants, or the ground should be determined and complied with. Safety, health and fire regulations should be observed.

"Since isopropyl alcohol is miscible with water in all proportions, small quantities may be flushed to a sewer system with large volumes of water, providing waste disposal regulations are complied with and providing the isopropyl alcohol is sufficiently diluted that flammable vapors are not formed in the sewer.

"Alternatively, small quantities of isopropyl alcohol can be disposed of by pouring on dry sand and then cautiously igniting it. The burning should be done in a remote area, safely away from buildings and other combustibles.

"Larger quantities of waste mixtures may be disposed of by atomizing the liquid into an approved type combustion chamber. "

### C. SURVEY ON INCINERATION

A fairly extensive, but by no means comprehensive, study of incineration methods and equipment was performed as an aid to assessment of this method of disposal. Twenty-four incinerator companies were contacted by us, and responses were received from seventeen. Of the seventeen that responded, at least three seem to have units compatible with the volumes and mix of liquid wastes that are anticipated at KSC. These units are physically somewhat smaller than the Thermal Research unit at CCAFS (see Report FR 1-3) and can handle a wide variety of chemicals, and incinerate solvents diluted with large amounts of water. Samples of the waste materials would be required by these companies in order to accurately determine the required incinerator size.

Two companies listed as environmental services were contacted; both provide engineering services for custom built equipment.

Incineration without scrubbing is a straightforward operation which many facilities perform routinely every day. Units are available at costs of \$10 K to \$20 K installed. These units are limited in what they can handle, in terms of environmental restrictions. They should not be used to destroy halogenated hydrocarbons or any toxic materials. For the KSC application they could handle

wastes such as oils, greases, non-halogenated hydrocarbons used in small volumes, and the still "bottoms" from the reclaiming of non-halogenated hydrocarbons.

Incineration with scrubbing is a much more costly operation — costly in terms of initial expense, installation and maintenance. Our findings to date show that these operations are normally limited to central (municipal or regional) waste disposal centers.

One manufacturer we contacted, Prenco Manufacturing Company of Madison Heights, Michigan, has installed units in Waukesha, Wisconsin; Waterbury, Connecticut; Russellville, Arkansas; and South Bend, Indiana. The unit is described in an article by the Mayor of Waukesha:

"Before construction of the liquid incinerator, many of the waste liquids were disposed of at Waukesha's landfill site where they became a potential water pollution hazard and created a fire danger. Wisconsin's new antipollution laws made landfill disposal of the materials even more unacceptable.

"The new system accepts virtually any petrochemical-type liquid industrial waste that is generated within the city limits — everything from automobile lubricating oils and greases to water-soluble cutting fluids and coolants, as well

as paint thinners, paint sludges, cleaning and degreasing solvents, and a wide range of other waste products. Only toxic materials, such as cyanide plating wastes, are refused.

"The incinerator system utilizes high-temperature chemistry to destroy liquid waste materials. Wastes from the system's mixing and holding tank are atomized by a stream of pressurized air and injected into the base of the unit's vertical refractory-lined retort which is preheated to 2200 F by an auxiliary fuel — in this instance, natural gas. Because of the extremely high temperatures in the retort, atomization and ignition of the wastes are almost simultaneous.

"As the waste rises in the retort, the high temperatures cause its molecules to dissociate into their constituent elements, and the availability of oxygen and the turbulent flow result in oxidation of the dissociated stream. Decomposition efficiency is increased through a system for ducting pressurized air from a point near the top of the retort through ports in the refractory. The air cone thus formed provides an afterburner effect that helps retain heat in the retort and saves fuel.



"In cases where the Btu content of the waste material is sufficient to maintain the retort at operating temperatures, auxiliary fuel is needed only during the initial preheating of the retort. An automatic control system continuously monitors retort temperatures and mixes additional auxiliary fuel with the waste as required during system operation.

"High Btu wastes, such as automotive lubricating oils, are mixed with low Btu wastes, like water-soluble coolants, to raise the average Btu level of the liquids burned. The end result is a material of higher Btu content that supports sustained pyro-decomposition without the use of auxiliary fuel, thereby reducing operating costs.

"As an added protection against air pollution . . . . . an auxiliary water scrubbing system was specified. The scrubber is hooked to the output of the pyro-decomposition system to prevent emission of any solid particles not decomposed in the retort, such as those from metallic plating wastes. One of the sewage treatment plant's settling tanks provides a ready source of water adjacent to the unit.

"When the scrubber is required, water is circulated from the tank, through the scrubber, and back to the tank. The scrubber provides for many of the unknown factors that may develop.

"Advance planning also led to the design of a "mini" holding tank for use by small firms or haulers. There is the possibility that some users will deliver waste in 55-gal drums, and it is a little difficult to empty a full drum of liquid into a 4-in. line. To allow for this eventuality, the Department of Public Works obtained a 275-gal residential-type fuel oil tank and laid it on its side. The side of the tank was replaced with a hinged top. Waste in drums can easily be emptied into the tank, then piped to the 10,000-gal holding tank.

"To protect the entire system against rags or other foreign objects, a double screen was welded over the drain leading from the 275-gal tank to the main storage tank. It is a simple matter for the hauler or operating personnel to remove any obstruction. " <sup>2</sup>

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<sup>2</sup> Paul Vrakas, "Liquid Incineration System-Municipal Solution for Industrial Waste Disposal." Plant Engineering, September 6, 1973.

The Prencos unit installed in South Bend, Indiana, has a capacity of 36,120 gallons per week, and is adaptable for heat recovery with maximum heat release of 28 million Btu per hour; it is 35 feet tall, weighs 47,000 pounds, and requires a 20' by 38' pad. Maximum operating temperature is 3000 F, well within the danger zone for NO<sub>x</sub> formation (see FR 1-3). Support equipment includes an on-site waste storage system with agitation and preheat, preheating of combustion air, an "EPA-approved" scrubbing system, and automatic remote control operation.

This unit cost is in the range of \$100 K with smaller units available in the price range of \$50 K. Their effectiveness is reported as 70 parts per million. These units can be cycled on and off; however, most companies save the material until a full load is stored and then incinerate at a slow rate to minimize cycling.

Heat recovery from this waste disposal technique is in vogue with the heat used either directly or to generate electricity.

Another manufacturer contacted was Envirotech Systems Inc. of San Francisco, California, whose BSP Industrial Thermal Systems Division manufactures a steam atomizing liquid waste burner known as the "Hydro" burner. The operation of this unit

is described in the following quotation from their advertising material:

"Because of its design, the Hydro Liquid Waste Burner takes advantage of normal radiation losses through furnace fronts and uses this energy to vaporize the material being burned. Atomizing steam or air used in the Hydro process is superheated by the radiant heat of the flame. Under normal operating conditions, the pressure of the atomizing steam or air supplied to the Hydro Burner should not be less than 150 PSIG for steam or 100 PSIG for air. The flame length is governed by the air or steam pressure to the burner superheater. Normal operating range of the Hydro Burner superheating System will be between 800°F. and 1200°F. Higher operating ranges are available where required by the nature of the waste material to be burned. The pressure at which the steam or air enters the burner superheater is determined by the operating conditions.

"Primary air for combustion is induced through the center of the nozzle and is thoroughly mixed with the waste liquid and superheated steam or air. This same action occurs while burning natural gas through the combination burner nozzle. Primary air for combustion is controlled

by the Hydro nozzle making it possible to reduce the excess air required. The waste liquid or gas being consumed is preheated and vaporized before it reaches the combustion zone of the burner. The ring at the nozzle outlet is in a negative pressure zone during the burner operation, making it possible to operate with relatively low supply pressures, even with heavy viscous materials.

".... it is possible to burn many types of liquid waste material previously considered impossible to incinerate, including waste liquid emulsions containing up to 50% non-combustibles.

"Heart of the liquid disposal system is its patented nozzle/superheater coil which assures intimate waste/fuel mixing, atomization, high velocity shearing and efficient heat transfer. There are no moving parts in the assembly. This nozzle is virtually clog-free even when burning wastes containing solids. In addition, it can handle wastes with wide viscosity variations and requires minimum maintenance. This nozzle is essentially a tube within a tube. The central core passageway is surrounded at the downstream end by a narrow annular orifice. In turn, it is surrounded by a larger annular orifice. Steam enters the superheater coil

where it is superheated, using radiant heat from the flame. Steam enters the nozzle inlet and flows at near sonic velocity through the narrow annular orifice. The steam creates a negative pressure area throughout the central core passageway, drawing primary air and, when required, gaseous fuel into the combustion zone.

"As liquid waste enters the larger annular orifice from the inlet, the superheated steam traveling at high velocity continuously shears and disperses the waste. This violent action, combined with the release of heat energy from the steam, shears the liquid waste breaking it into a fine mist or vapor. Primary air and gaseous support fuels (if required) mix throughout the central core passageway, producing a thorough mixture of air, waste, and fuel. The pre-heated vaporized mixture passes through the superheater coil and the turbulator plate and then into the afterburner chamber. Ignition of the mixture takes place within the coil and the burning extends into the afterburner chamber. As the flame enters the afterburner chamber, a cooling sleeve of excess air may be introduced to rapidly drop combustion temperature while shaping the flame. This reduces  $\text{NO}_x$  production and extends the life

of the refractory lining. In the afterburner, burning gases are retained to ensure complete combustion. "

These descriptions are included in our report for the sake of presenting some idea of the nature of modern liquid waste incineration systems, rather than with the intention of singling out particular manufacturers. The field is a large and very competitive one, and the two manufacturers referred to here were selected solely on the basis of the fact that they sent us very useful technical information in response to our inquiries, written in a style that was sufficiently professional and restrained that we felt it appropriate for inclusion in our report. A list of thirteen liquid waste incinerator manufacturers provided to us by the State of Florida Department of Pollution Control is included in an Appendix to this report.

#### D. SURVEY ON RECLAMATION

There are two ways one can approach the reclamation of solvents. The first is to set up an in-house facility to recycle one's own waste solvents and the other is to have it done by a material scavenger. The in-house facility is the recommended approach for small ( < 10 drums per month) quantities. The advantages are:

- (1) The dollar savings are greater due to the reduced cost of hauling and the eliminating of service charges.
- (2) The control of the entire program is much better, particularly in the area of schedule and final disposition of distillation "bottoms".
- (3) Each recovery problem has a unique solution which can be more easily optimized by the generating agency. The outside reclaimers must, of necessity, have the generating agency conform to their system.
- (4) The potential for obtaining material of high enough purity to enable the generating agency to reuse the material is much higher.

The disadvantages are:

- (1) The large capital outlay to get the program started.
- (2) The cost of administering the program is a little higher.



A few typical suppliers of stills for setting up an in-house facility were contacted and their literature was reviewed. One of these companies, Interdyne, of Indianapolis, Indiana, sells a unit capable of distilling and recovery of all the solvents under consideration. The smallest unit sells for between \$8 K and \$10 K with a capability of recovering 10 gallons per hour. Baron Blakeslee, of Chicago, Illinois, manufactures solvent recovery stills including units designed for halogenated solvents. Their MRW 20 is the unit presently being used for Freon recovery at KSC.

There are a number of solvent reclaimers in the Southeast, including the following who were contacted by us:

(1) M & J Solvents Co.

P. O. Box 19703, Station N

Atlanta, Ga. 30325

Mr. Don McQueen (404) 355-8240

Data Sheet: on file.

Users: (a) American Lacquer Solvents in Tampa.

Mr. Henderson (813) 236-5594.

The solvents, mainly ketones and acetates (paint thinners), are mixed. They sell them to M & J at prices ranging from

5¢ to 20¢ per gallon. They do not buy back the solvents. They also distill 4-5 drums per day using a still they purchased from the Brighton Company in Chicago, Illinois.

(b) Poly Plastrex in Tampa.

Mr. Marick (813) 525-2173.

(2) Chemetrol

Box 11502

Charlotte, N. C. 28209

Mr. Bill Tourtellot (704) 588-3622

Specialists in reclaiming Freon recommended by Dupont.

(3) Erny Supply Co.

5406 59th Street

Tampa, Fl.

Mr. Leo Erny (813) 621-3487

This group reclaims a wide variety of solvents for use in the host of formulations (waxes, cleaners, etc.) that they sell. The disposal of bottoms (particularly those with toxic substances) may not meet the EPA standards.

A catalog is in the file.

(4) SCA Services in Tampa.

Mr. Ty Hartley (813) 884-8436

This is a sales office and facility for solid waste. However, SCA is a major reclaimer of liquid wastes. They supplied literature on the analysis and packaging of liquid wastes. Their main operation (Chemetrol) is in Model City (outside Buffalo, N. Y.).

Mr. Walter Watson (716) 754-8231.

(5) Arvec Chemical Co. in Atlanta.

Mr. D. Johnson (404) 942-4332

Users: Harris (formerly Radiation, Inc.) in Melbourne, Fl. Contacted Mr. Phil Dennough who said the service was good; however, the volume was so low they are not using the service.

(6) Gold Coast Oil Co.; Miami, Fl.

Mr. Joe Bowen (305) 264-2761

At the present time they were interested in all of our materials except the Freon.

Users: Piper Aircraft in Vero Beach.

Mr. Aten (305) 567-6361 (X 435)

(7) Browning Ferris Industries of Mobile, Ala.

Mr. Carl Butler (205) 661-1036.

Mr. A. J. Kennard.

This company claims to be the largest  
of the solvent reclaimers.

Some of these operations (both reclaimers and users) were  
visited by us; trip reports are included in an Appendix.

Other companies to which we were referred by the State  
of Florida Department of Pollution Control are listed in an  
Appendix.

Reclamation of waste solvents is a method of "disposal"  
especially dependent on the system and procedures used in the  
collection of the wastes; this subject is treated in detail in the  
final section of this report.

## CHAPTER III

### Applications Studies

The following subsections present the results of four experimental studies that were undertaken to investigate specific questions regarding the disposal of these contaminated waste materials at Kennedy Space Center. The first of these experimental studies treats the biodegradability of ethylene glycol and isopropyl alcohol; the remaining three studies are concerned with removal of hypergolic propellant contaminants from the solvents of interest.

#### A. TESTS ON BIODEGRADABILITY

As part of the Phase Four work, a short program was initiated to determine the feasibility of degrading certain unwanted solvent wastes by biological means, so as to convert to non-toxic end products. It was reasoned that with pond availability for destruction of MMH, it was only a step away to try the same method for other materials. The principles discussed in the preceding section apply here. Ethylene glycol and isopropanol were selected for study, although methyl ethyl ketone could be similarly treated. Chlorinated and fluorinated solvents, although biodegradable (if slowly), may result in some toxic end products.

A laboratory set up similar to that used for MMH, as shown in Figure 1, was used to perform the biodegradability tests. In a test, two bubblers containing 400ml of approximately 1000 to 2000 ppm of the solvent were aerated at 10ml/minute. One bubbler was inoculated with a small amount of sewage water, one was not. Periodically 5ml samples were withdrawn and analysed for residual solvent utilizing the COD Technique. The low air flow provided sufficient dis-

solved oxygen and yet minimized evaporation of water or volatile solvent. In these preliminary runs, the effect of evaporation was ignored. For purposes of these tests the COD values expressed as mg/l, were assumed to be roughly equivalent to ppm of the solvent. A  $\text{Cu}^{++}$  catalyst was not used, thus oxidation of solvents by air was insignificant.

The results of the tests appear in Table II. In Test 1, 19% reduction of ethylene glycol occurred in 20 hours. IPA reduction was negligible. The effects of water evaporation are evident from the higher figure.

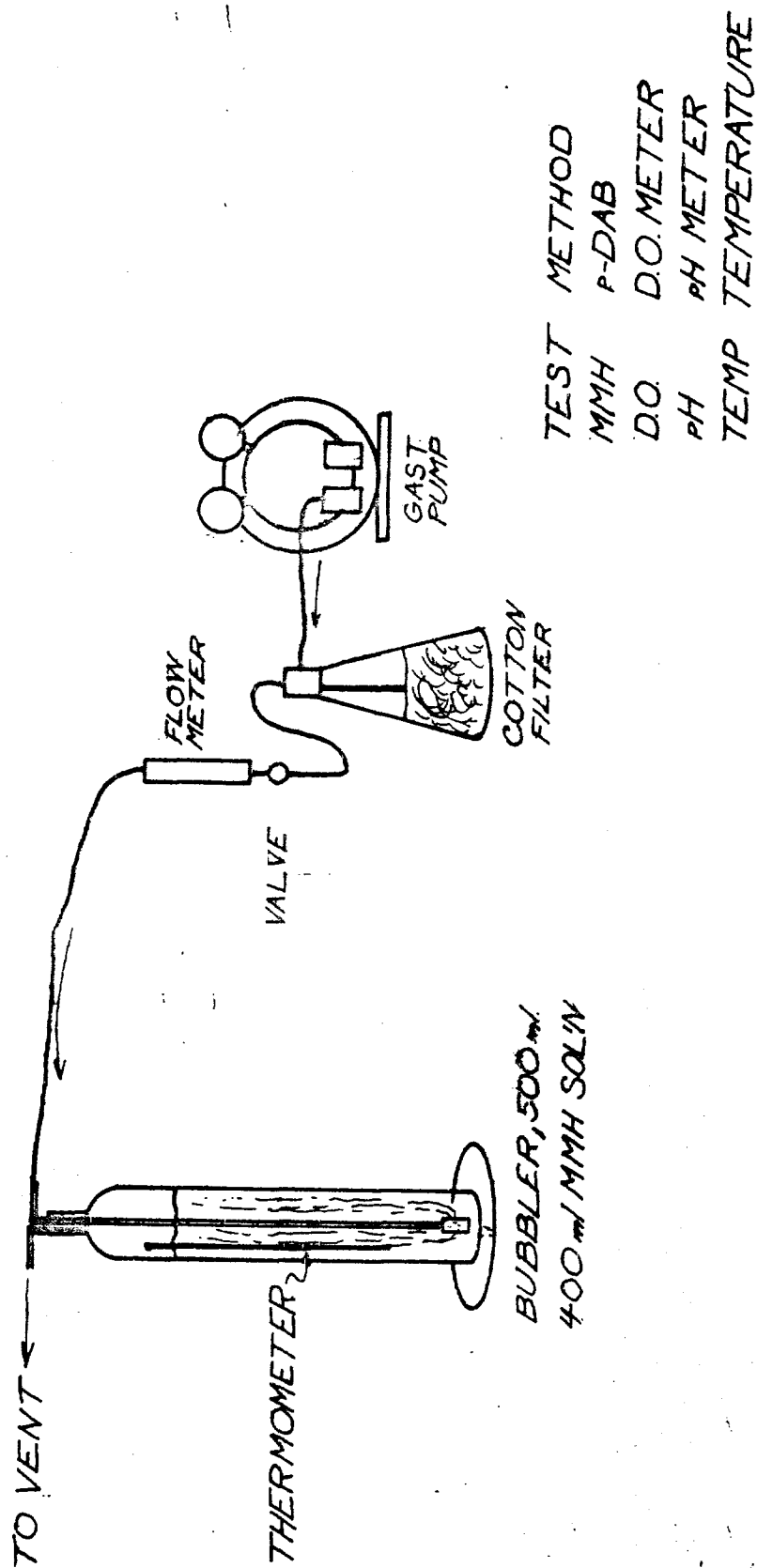


Figure 1: SCHEMATIC SHOWING LAB SET-UP FOR BIODEGRADABILITY TESTS

Table II  
RESULTS OF BIODEGRADATION TESTS

#	Time	Ethylene Glycol, ppm		IPA, ppm		% Reduction
		No Seed	Seeded (.5 %)	No Seed	Seeded (.5 %)	
Test 1	Initial	1080	1050	1870	1810	EG: Essentially zero unseeded 19% seeded. IPA: Essentially zero in both cases
	20 hrs.	1140	950	2000	2030	
Test 2	Initial	---	---	---	4280	----
	72 hrs.	---	---	---	2060	47%
	96 hrs.	---	---	---	1870	56%
Test 3	Initial	---	(.25% Seed) 1835	---	---	---
	24 hrs.	---	1330	---	---	27%
	72 hrs.	---	0	---	---	100%
Test 4	Initial	1280	1280	1800	1890	Very little Re- duction in both seeded and un- seeded runs.
	24 hrs.	1210	1150	1840	1890	
	48 hrs.	1290	1290	1730	2030	



In Test 2 about 56% reduction of IPA occurred after 96 hours, which is relatively slow for a seeded sample.

In Test 3 100% reduction of ethylene glycol occurred in about three days on a seeded sample.

In Test 4 there was little if any reduction of ethylene glycol or IPA in either seeded or unseeded runs. This result can only be attributed to the use of a "dead" seed, which actually was a week old and therefore not too virile. Further, no attempt was made in any of the four runs to produce optimum growth conditions for the bacteria such as pH, suitable trace elements, nutrients, temperature, etc. It might be said the inoculum was not acclimated.

#### Conclusions

(1) It was verified that ethylene glycol and IPA are both biodegradable, IPA being more resistant than ethylene glycol. (2) In Test 4, where the seed was believed "dead", biodegradation was negligible. (3) More studies are needed to optimize this method before comparisons can be made to the other candidate methods of destruction.

## B. NO<sub>X</sub> ADSORPTION FROM TRICHLOROTRIFLUOROETHANE

An experimental investigation was made of the purification of Freon 113 (Trichlorotrifluoroethane), contaminated with  $N_2O_4$ , by adsorption on prepared Kieselguhr.

The precision cleaning agent, Freon 113, used for cleaning space vehicle components, is generally recovered by batch distillation at KSC. In the batch type distillation operation, as practiced at KSC, the  $N_2O_4$  is first neutralized with caustic and then the freon distilled.

A problem may exist in performing a continuous distillation operation when the freon is highly contaminated with  $N_2O_4$  from the accumulation of  $NO_X$  in the condenser. With the projected increase in usage of freon for the shuttle program, a continuous system of distillation can provide greater capacity with more economy. This study was conducted to develop a method of reducing the  $NO_X$  concentration in freon to be recovered so as to permit a continuous distillation system operation. The method investigated was to run the highly contaminated freon through a column containing the prepared Kieselguhr. This preparation consisted of treating Kieselguhr for about one hour in 10% NaOH solution, leaching out excess NaOH with 5-6 changes of water and drying in an oven overnight. The dried powder was lightly packed into columns 11 1/2 inches high. Measured quantities of  $NO_X$ -contaminated freon were passed by gravity through the column and the leached freon analyzed for  $NO_X$ . The results appear in Table III. There was approximately a 100-fold decrease in the amount of  $NO_X$  in the freon. The freon initially containing 1455 ppm  $NO_X$  contained 16.6 ppm after passing through the column of Kieselguhr, probably due to the high affinity of freon for  $NO_X$ . A taller column or neutralization prior to distil-

lation is indicated.

Stripping  $\text{NO}_X$  by blowing an inert gas, such as  $\text{GN}_2$ , through the freon can be expected to remove most of the dissolved  $\text{NO}_X$ . Stripping would be particularly simple and inexpensive to perform because of the low boiling point ( $21.1^\circ\text{C}$ ) of  $\text{N}_2\text{O}_4$ . This operation would be a preliminary step, prior to a final purification step -- either distillation, or adsorption using a column of Kieselguhr.

Stripping involves bringing a liquid containing a dissolved gas into contact with an inert gas in order to remove (strip) the dissolved gas from the liquid. Countercurrent flow of liquid and inert gas is usually employed. High temperature and low pressure are favorable.

In practice, the equipment required for stripping  $\text{NO}_X$  would consist of an absorption tower, either the bubble-cap or packed type similar to gas absorption towers, a means for warming the freon and a means for condensing the vaporized freon, and a small scrubber to capture the evolved  $\text{NO}_X$  gas. The partially purified freon can then be distilled in a simple still for final purification.

Table III

	NO <sub>X</sub> Concentration (ppm)		Percent Reduction
	Initial Solution	After passing through column	
Test 1	147	1.42	99.05
Test 2	1455	16.6	98.86

### C. AN ION-EXCHANGE METHOD FOR PURIFYING MMH-CONTAMINATED ISOPROPYL ALCOHOL

An ion-exchange method for purifying contaminated IPA was investigated and is described herein. The requirement of IPA used to decontaminate the shuttle module will be approximately 5,000 gallon/week at a cost of \$1.10/gallon in tank car lots. This represents a weekly cost of \$5,500. Solvent recovery is indicated as a cost reduction and resource conservation measure. Simple distillation for removal of the MMH is not feasible due to the closeness of the boiling points of the two liquids ( $< 5^{\circ}\text{C}$ ). Batch rectification, as a method for separating the MMH contaminant from the IPA, was considered uneconomical due to the high initial equipment cost relative to the volume of the solvent to be recovered.

The method consists of two steps. First, the contaminated IPA is treated with a cationic exchange resin to adsorb the MMH, usually present in several hundred to several thousand ppm concentrations. The treated IPA is then distilled to remove trace impurities such as particulates and color. The quality of purified IPA should nearly meet the federal specification # TT-1-735a except possibly for the trace water content of grade A (0.10%). This deficiency should not interfere with its reuse for preliminary rinsing purposes. The used resin can be regenerated after becoming nearly saturated with MMH by the normal HCl-regeneration procedure.

The procedure followed in the laboratory was as follows. Two resins were tried. Fifty grams of Dowex 50W-X8 resin or Dowex AG 50W-X10 (20-50 mesh) were placed in individual 500 ml separatory funnels, containing cotton plugs at the bottoms. 250 ml portions of impure IPA were added to each. The funnels were shaken 1/2 minutes at 10 minute intervals, 6-7 times. The solvent was

drained through the cotton plug into bottles. A second portion of impure IPA was again added to the same resin and shaken/drained as before. The resin-treated elutriants were distilled in a standard distillation apparatus. Samples of IPA were analyzed for MMH by the p-Dimethylamino Benzaldehyde Method with results as shown in Table IV.

The elutriated IPA still contained small quantities of MMH. The light yellow color probably originated from leaching the ion-exchange resins. The color was much fainter in the 2nd elutriation.

After distillation all four batches were colorless without detectable MMH. Thus, complete MMH removal was demonstrated by this method.

In practice a measured quantity of IPA would be run through a resin-filled column to below the break point of the resin. A batch type still could be utilized for distilling the treated IPA. If desired, the distilled IPA could be labelled "recovered IPA" for restricted use.

Should it become necessary, further laboratory work can be performed to optimize the process, minimize the cost, or to provide additional design information.

Table IV

SAMPLE	MMH	COMMENTS
Contaminated IPA	314	
1st Elutriant:		
a. Dowex 50W-X8	1.0	Straw Yellow Color
b. Distilled	0.0	Colorless
c. Dowex AG 50W-X10	0.3	Light Straw Yellow
d. Distilled	0.0	Colorless
2nd Elutriant:		
a. Dowex 50W-X8	0.9	Light Straw Yellow
b. Distilled	0.0	Colorless
c. Dowex AG 50W-X10	0.7	Very light yellow color
d. Distilled	0.0	Colorless

#### D. A NEW METHOD FOR REMOVAL OF MMH FROM ISOPROPYL ALCOHOL

At the present time, it is envisaged that isopropyl alcohol (IPA) will be used to flush lines and tanks contaminated with monomethylhydrazine (MMH) in the Shuttle Program. In view of the fact that as much as 5,000 gallons of IPA will be used after every launch, an investigation of feasible methods to recover the contaminated IPA was undertaken. It is recognized that any method chosen must take into account the toxicity and carcinogenicity of the MMH contaminant.

Simple distillation of IPA was eliminated from consideration since IPA and MMH have similar boiling points ( $82.4^{\circ}\text{C}$  and  $87.5^{\circ}\text{C}$  respectively). Removal of MMH from IPA using ion exchange resins is effective, as has been shown in the preceding subsections. However, there are severe disadvantages to this method:

- 1) The expensive ion-exchange column must be recharged after use.

This involves additional labor and handling of toxic MMH.

- 2) The MMH removed from the column in the recharging operation must subsequently be destroyed.

- 3) A subsequent distillation step to purify IPA would still be necessary.

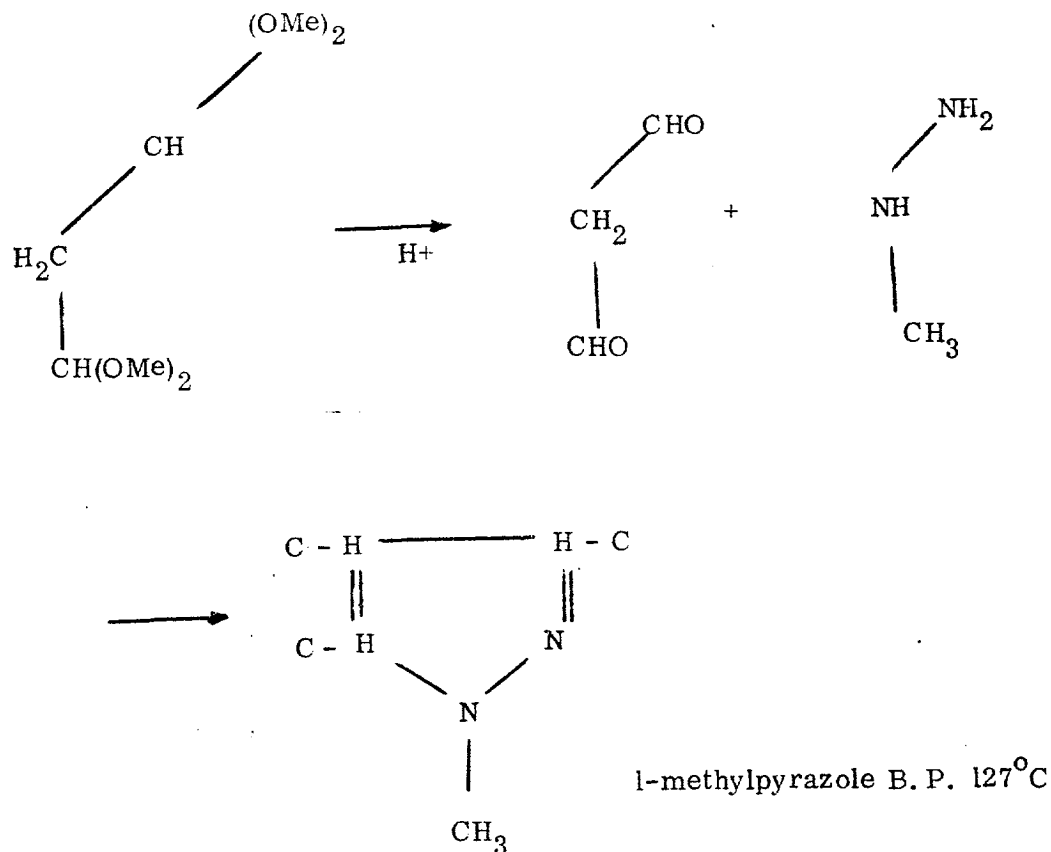
Therefore, a method involving conversion of the MMH contaminant to a harmless, relatively high boiling derivative followed by subsequent distillation was considered.

Hydrazines are very versatile compounds which can undergo many reactions. However, the most common derivatives are hydrazine salts, hydrazones, and pyrazoles. Hydrazine salts were ruled out because they tend to explode and would still be toxic. Hydrazones were ruled out because they are relatively unstable and could hydrolyze during the distillation to regenerate



toxic MMH. Pyrazoles, however, have none of these disadvantages. They are stable and non-toxic.

1-Methyl pyrazole is readily synthesized from the commercially available 1,1,3,3-tetramethoxy propane (TMP, B. P.  $183^{\circ}\text{C}$ ) and MMH in the presence of acids.\* This type of synthesis is successful with almost any 1,3-dicarbonyl compound and any mono-substituted hydrazine.



\* Acheson, R. M., An Introduction to the Chemistry of Heterocyclic Compounds, Interscience Publishers Inc., New York, 1960, P. 263.

Pyrazoles are remarkably stable to oxidation and acid hydrolysis and these properties are consistent with the presence of a great deal of aromatic character.

Therefore a laboratory program was undertaken to determine the feasibility of reacting TMP with 0.01M MMH in IPA followed by subsequent distillation. The procedures were conducted as follows:

1,1,3,3,-tetramethoxy-propane (TMP) was added to 100ml of 0.01M MMH in isopropyl alcohol (IPA). One drop of concentrated sulfuric acid was added. The solution was refluxed and then distilled (80-85°C). The clear distillate containing pure IPA was analyzed for MMH. % Recovery IPA = 85%.

The conditions and results are as shown in the following table.

Reaction Condition #	Wt. of TMP	Molar Ratio TMP:MMH	Reflux Time (Hr.)	MMH in Distillate (ppm)
1.	0.324	2:1	0.5	0
2.	0.200	1.2:1	2.0	0

The assay method used to determine MMH was the DAB method as outlined below:

#### Assay Method

1. Prepare 5ml DAB reagent.
2. 2ml of IPA containing MMH.
3. Q.S. to 25ml with 1 M HCl.
4. Allow to stand 0.5 hr.
5. Read at 485  $\lambda$ .
6. Subtract a reagent blank prepared by using 1ml H<sub>2</sub>O in place of IPA solution.

#### DAB Reagent

1. 1 g. p-Dimethylaminobenzaldehyde
2. 10 ml concentrated hydrochloric acid
3. Dilute to 100 ml with methyl alcohol

#### Basic Costs

The cost of 1,1,3,3-tetramethoxypropane (TMP) is:

1. \$3.50/lb - less than one drum
2. \$1.93/lb - one drum to 50 drums
3. \$1.81/lb - truckload
4. \$1.78/lb - tank car

In order to process 5,000 gallons (19,000L) of IPA containing 0.5g/L according to the faster Reaction Condition #1 approximately 150 lbs. of TMP would be required. Therefore, the basic material cost per batch would be  $(150) (\$1.93) = \$290$ . In the case of the slower Reaction Condition #2 approximately 90 lbs. of TMP would be required, yielding a basic material cost per batch of  $(90) (\$1.93) = \$174$ .

## CHAPTER IV

### Evaluations and Recommendations

#### A. GENERAL DECISION MATRICES

Decision matrices covering the possible solvent disposal methods for the six materials of interest were prepared. Ratings from zero to ten were made on the basis of the considerations presented in the preceding sections of this report. High ratings indicate a practical and desirable disposal method, in terms of environmental impact, safety, and cost. These ratings are presented in Table V for cases where the waste materials are not contaminated with hypergolic propellants, and Table VI for cases where they are contaminated with hypergolic propellants. Economic considerations are treated in more detail -- as a function of quantities involved -- in the following subsections.

TABLE V  
DECISION MATRIX  
SOLVENTS UNCONTAMINATED WITH FUEL OR OXIDIZER

SOLVENT (TLV)	RECOVERY BY DISTILLATION	BIO-DEGRADATION HOLDING POND	INCINERATION	DILUTE AND ADD TO SEWER OR STREAM -OR OCEAN	SIMPLE EVAPORATION
1. IPA (400 ppm)	10	10	10	10	10
2. FREON 113 (1000ppm)	10	0	0	0	5*
3. ETHYLENE GLYCOL (200 ppm)	10	10	10	8	0
4. METHYLENE CHLORIDE (500 ppm)	10	7	5*	0	3
5. TRICHLOROETHY- LENE (100 ppm)	10	6	5	0	2
6. MEK (200 ppm)	10	10	10	9	7

\* Undertermined future regulations.

TABLE VI

## DECISION MATRIX

## CONTAMINATED SOLVENTS

SOLVENT	RECOVERY BY DISTILLATION	BIO-DEGRADATION HOLDING POND	INCINERATION	DILUTE AND ADD TO SEWER, STREAM, OR OCEAN	SIMPLE EVAPORATION
1. ISOPROPYL ALC contaminated with MMH (<10%)	10*	0	7	0	0
2. FREON 113 plus $N_2O_4$ (<10%)	10* (Requires 5 ppm limit on $N_2O_4$ )	0	0	0	0
3. TRICHLOROETHYLENE plus HC Lubricant (<10%)	10 (residue to Group I)	2	5*	0	0
4. MEK plus Lacquer Residue (<10%)	10	8	8**	0	3
* Must complex MMH or neutralize first. ** Requires Scrubber ** Requires particulate remover and scrubber					

## B. ECONOMIC CONSIDERATIONS

An estimate of the possible saving on solvent recovery can best be made by the user who is in a position to factor in the cost elements. Steps involve determining the cost of annual solvent consumption and comparing it with the cost of solvent recovered, after deducting operating and amortization cost of the recovery unit. Obviously, to make recovery worthwhile a minimum volume of waste solvent is required to operate above a break-even level. The more expensive a solvent, generally, the smaller the volume necessary to make in-house recovery attractive. The estimates in Table VII are suggested as the minimum volumes, but are subject to change as conditions change. It should be noted that recovery might be the method of choice even if no cost savings is possible, because of the cost - economic, environmental, or otherwise - of the other disposal methods.

Table VII carries this concept a step further, and presents more detailed recommendations. No consideration was given in the preparation of this chart to the new method developed by us for the removal of MMH from IPA, although we believe this method is an attractive possibility for a wide range of cases.

TABLE VII  
ESTIMATED BREAK-EVEN QUANTITIES FOR IN-HOUSE RECOVERY

Solvent	Approx. Avg. Weekly Vol., Gal.	Approx.* Annual Vol., Gal.	Recovery Process
Freon	200	10,000	Distillation
Isopropanol	500	25,000	Distillation Drying
Methylene Chloride	1,000	50,000	Initial Water Separation and Distillation
Trichloro- ethylene	1,500	75,000	Initial H <sub>2</sub> O Separation followed by Distillation
Methyl Ethyl Ketone	1,000	50,000	Distillation
Ethylene Glycol	1,000	50,000	Distillation



TABLE VIII

## SUGGESTED DISPOSITION OF SOLVENTS BASED ON VOLUME AND ASSAY

Solvent	Volume	Assay	Disposition			
			Recover**	Incineration	Commercial Reclaimer	Other
FREON	> 200 gal/wk	> 97%	X			
	200-100 gal/wk	"	TBD		TBD	
	< 100 gal/wk	"			X	
IPA	Any quan.	< 95%				May require special treatment
	> 500 gal/wk	Up to .5% MMH				
	100-500 gal/wk	Up to .5% MMH	X			
	< 100 gal/wk	Up to .5% MMH			X	
	> 500 gal/wk	< .5% MMH		X		Dilute and Aerate or Biodegradation in Pond
	Any Quan.	Up to 5% H <sub>2</sub> O	X			
	Any Quan.	> 5% H <sub>2</sub> O		X	X	
		.5% MMH & up		X	X	Alt. Dilute and Treat by a Suitable Process

TABLE VIII (continued)

Solvent	Volume	Assay	Recover**	Incineration	Commercial Reclaimer	Other
METHYLENE CHLORIDE	> 1000 gal/wk < 1000 gal/wk	> 95%*	X		X	
TRICHLORO-ETHYLENE	> 1500 gal/wk < 1500 gal/wk Any Quan.	> 95%* > 95% < 95%	X		X X	
MEK	> 1000 gal/wk < 1000 gal/wk	> 95%	X		X	
ETHYLENE GLYCOL	> 1000 gal/wk < 1000 gal/wk	> 95%	X		X	Alt: Bio-degrade

\*Excludes water which separates easily

\*\*Does not include treatment of IPA with tetramethoxy propane, which might be desirable with a wide range of applicability.

### C. RECOMMENDED PROCEDURE FOR HANDLING SOLVENTS PRIOR TO RECLAMATION

The purpose of this subsection is to define the parameters of a recommended system for the recovery of solvents, for cases where recovery is the disposal method of choice. It identifies technical considerations in defining these parameters and in some cases shows specific examples for clarity. It is not our purpose to present a complete system or even a comprehensive format.

The system should clearly delineate:

- (1) The responsibility of the controlling agency such as a "Liquid Waste Disposal Committee".
- (2) The responsibility of the using department.
- (3) The responsibility of the material handling departments including the receiving and shipping departments.
- (4) The decision making procedure including any analysis and how the analysis is made.

Each of these considerations is discussed in the paragraphs below.

#### Liquid Waste Disposal Committee

The committee should be established with technical representation from the group that will perform the analyses, the maintenance department, and a pollution specialist. There should also be representation from purchasing to insure a continuous updating of price and availability, and from the group or groups that perform the receiving and hauling operations. A rotating member from one of the using departments might also be useful. This would set the committee at a maximum size of about seven members.

A general disposal technique should be established for each solvent based

on cost, availability, and overall usage. A list showing these techniques for each solvent should be prepared for the use of the group responsible for affixing initial disposal labels to barrels of waste material as they are filled or received.

The committee should support the various user organizations in determining the final disposition based on their usage and the contaminants involved. A solvent disposal form should be prepared; see the following page for an example of the sort of form that is indicated.

The committee should issue general instructions regarding the collection and analysis forms, including the forms themselves.

The committee should issue specifications and instructions on the packaging and identification of liquid waste products.

#### Responsibility of the User Organization

This responsibility includes procedures for dispensing the waste material into containers for collection. The using department would also have the responsibility of administering the data tags on each drum of spent solvent. The responsibility for working with the committee on generating and maintaining records must be well defined. The using department will definitely influence the final disposition of the spent solvents based on quantities and variety of solvents used.

Dept. No. 2453

Form No. 7427

Rev. A

Dtd. 7-6-74

Item No.	Material Description	Spec. No.	Use	Contaminant	Disposition	Code
1	MEK Ind. Grade	KSC 0120	Paint Thinner	Paint Non Lead	Reclaim	R101A
2	IPA (95%) C. P. Grade	KSC 0527	Hypergol Flush	MMH < 1%	Reclaim	R104A
3	TCE C. P. Grade	KSC 0400	Parts Degreasing	Ni Salts < 1%	Reclaim	R106B
4	TCE C. P. Grade	KSC 0400	P. C. Board Degreasing	Flux	Reclaim	R106B
5	TCE Ind. Grade	KSC 0402	Machine Shop	Oils	Reclaim	R106A

Item No. - Self Explanatory

Material Description - Chemical Name and Grade

Spec. No. - Purchasing Specification for Material

Use - Brief Description of the Use of Material

Contaminant - Estimate Type and Quantity of Contaminant

Based on Use and Typical Analysis if Necessary

Sufficient Data to Complete Fig. 2 Without Analysis

Whenever Practical.

APPROVED: \_\_\_\_\_ Dept. Head

\_\_\_\_\_ Purch.

\_\_\_\_\_ Eng.

Disposition - Reclaim, Incinerate or Dump

Code - Quick Identification Tag for the Bulk Material  
Handlers

RECOMMENDED FORMAT FOR A DEPARTMENTAL WASTE MATERIAL DISPOSAL FORM

### Responsibility of the Material Handling Organization

The responsibility for solvent reclamation should start at the receiving dock where all the solvents are labelled as to disposal techniques based on price and availability. With the prices of chemicals increasing as they are, most of the drums will probably receive a reclaim label. Only the specialty chemicals used in low volumes will get an incinerator or dump label. These labels should key the disposal technique and a coded number to identify the solvent. The user will modify this label by adding a final disposition letter to indicate "buy-back" or "sell to material scavenger" and on some occasions, where the concentration is low or the contaminants undesirable, he will change the label. Some examples:

R103 Reclaim IPA (Labelled at Receiving)

R103 B Reclaim IPA (B added by Using Dept. indicated it will buy back the IPA)

I103 Incinerate IPA (Label changed by Using Depart. as IPA contaminated with heavy oils and grease)

The material handlers that haul away the used solvents will check the label code letters against a predetermined destination and bring the material to that point which will be a storage point or a final disposal operation.

### The Decision-Making Process

The decision process should be a simple one, with the majority of decisions made by specialists prior to actual need. For example, the establishment of a solvent waste committee provides the technical experts in chemical analysis and pollution control. The using department provides engineering expertise on the process that the solvents are used in. These three can make the best decision on the collection and disposal of solvents prior to the solvents'

being used. They can define lots and fill out the analysis sheet with a minimum of effort, based on their collective knowledge. They also provide the code for the last column of the Waste Disposal Form.

In the case of solvents of unknown origin, the full analysis described below is required.

### Physical Analysis

It will be necessary to perform a physical analysis of the material and verify that it is suitable for reclamation. Items that must be included are:

(a) Physical state - Is the material solid, semi-solid or liquid? Obviously the first category is not reclaimable and the analysis stops.

(b) Viscosity - The major requirement for this analysis is to determine that the material is capable of being pumped. Roughly, a motor oil SAE 30 or less is low viscosity, oils greater than SAE 30 are medium, and grease and sludge are high. Again a high category is not suitable for recovery and the analysis stops.

(c) The percentage of solids by weight should be checked and recorded. If the percentage is greater than 10, then the material is probably not suitable for reclaiming.

(d) Composition - The composition should be checked for layering. After the sample is selected, the number of layers is recorded and the percentage of solids in each layer is estimated. Categories of  $<10\%$ ,  $10-30\%$  and  $>30\%$  are adequate estimates. Samples with  $>30\%$  (by volume) suspended solids are probably not regarded as reclaimable. The sample is then allowed to sit overnight and the layering rechecked and an estimate made of the

amount and position of each material if the solvent is multilayered.

(e) Specific gravity should be checked and recorded. This data provides a means of calculating the weight for shipment and is a rough check on the composition.

(f) The flash point should be checked and recorded. This data is important to the hauler.

(g) The heat value will be recorded, based on the analysis and Tables.

### Chemical Analysis

#### (a) Major Constituent

The first analysis is to validate that the material on the tag is the major constituent. The % water is checked and recorded; a requirement might be that it must be less than 50%. The concentration of major constituent is checked and recorded—a requirement of over 50% might be made here. If either of these conditions is not met then the material is unsuitable for reclaiming and the analysis stops.

(b) The pH is checked and recorded.

(c) % Cl is determined and recorded.

(d) % F is determined and recorded.

(e) At this point the analysis form is reviewed by a responsible engineer in the analysis group. Based on the analysis, and labels and source of material, he makes one of the following determinations.

- Material is mixed or contaminated and not suitable for reclaiming.
- Material is suitable, in which case the analysis will be continued



for acids, bases, metallics, salts, cyanides, carcinogens, or any other toxic or hazardous materials that might be in the spent solvent based on its past usage and storage.

#### Final Disposition

(a) Upon completing the analysis of the lot, the analysis is reviewed and signed by the responsible engineer in the analysis group. Any major discrepancies between label and analysis are reviewed with the liquid waste disposal committee.

(b) The analysis sheet is used by the purchasing department and his technical representative to negotiate with the reclaimer, if an outside reclaimer is involved.

#### D: GENERAL DISCUSSION OF IPA DISPOSAL ALTERNATIVES

Simple batch distillation without pretreatment of IPA containing a few tenths of a percent MMH is not feasible since the boiling points of the two constituents are too close to allow a thorough separation. Rectification of this mixture is not justified on the basis of the small volume of solvent and the greater initial outlay for equipment required to perform the recovery. Treatment with tetramethoxy-propane, the method presented at the end of Section III of this report, appears to be the best way -- and only economically feasible way-- of recovering IPA contaminated with MMH.

The presence of substantial amounts of water in the IPA presents a limitation. IPA and water form an azeotropic binary mixture containing 31.46 Mol %  $H_2O$  which boils at  $80.4^{\circ}C$  at 760 mm pressure. Thus, the MMH contaminated IPA also containing several tenths of a percent  $H_2O$  cannot be simply batch distilled to provide a distillate that will meet the TT-1-735 specification. To obtain a bone dry product, as required by this specification, treatment may be required with an appropriate desiccant, such as calcium sulfate, and even then reduction to 0.1%  $H_2O$  may not be possible without rectification. In many applications, however, such a low water content may not be necessary.

Disposal of low assay IPA wastes ( $< 90\%$  IPA) by sufficient dilution with water is usually satisfactory. Sufficient dilution in this case means to reduce the MMH below .5 ppm and alcohol below the 1000 ppm level. The diluted solution can be run through the normal drainage channels into the sewage system. IPA is biodegradable and the toxicity of highly diluted MMH will be minimal. An alternative, especially for higher assay IPA, is dumping into an evaporation basin located in an isolated and fenced off area. The maximum

amount treated at one time by this method should be limited to about one drum.

A third possibility is incineration, particularly of high assay IPA which may have a calorific value as high as 14,000 Btu/lb. Liquid waste streams which contain about 10,000 Btu/lb or more can usually be incinerated directly in a thermal burner without the requirement of an auxiliary combustion chamber.

#### E. STORAGE OF WASTE SOLVENTS

It may be advisable to store individual waste solvents for a period of one month or more until a volume of 5000-7000 gallons is accumulated, then to process it in house or sell to a reclaimer. This gallonage is considered a minimum quantity to handle economically. Occasionally, a 2000 gallon batch of a high priced solvent (Freon 113) can be sold or recovered for recycling.

Outdoor storage of waste solvents, especially if containing reactive impurities or substantial water, in excess of two months will cause solvent deterioration as well as container corrosion or leakage. Shed storage is expensive and a time limit of four to six months should be placed on the materials. Storage indoors in work areas is not advisable for substantial quantities.

## F. RECOMMENDATIONS AND CONCLUSIONS

(1) Solvents uncontaminated with fuel or oxidizer may all be recovered by distillation and used again, either in an on-site facility or at an off-site reclamation center. In many cases it will be most practical to store waste solvents until sufficient quantities accumulate for a reasonable distillation run.

(2) Isopropyl alcohol (IPA), ethylene glycol (EG), and methyl ethyl ketone (MEK) can be disposed of by addition to holding ponds which would allow bio-degradation.

(3) These three materials, (IPA, EG, and MEK) could also be incinerated without scrubbing, under proper conditions.

(4) Smaller amounts of IPA (less than one drum) can be disposed of by addition to sewer, stream, or ocean or simply allowed to evaporate in the atmosphere.

(5) Isopropyl alcohol contaminated with MMH must be treated in such a manner as to first complex or neutralize the MMH before distillation. One method would involve running the contaminated IPA through an ion exchange column to remove the MMH. A preferred method involves chemical conversion of the MMH to any environmentally innocuous heterocycle followed by distillation and recovery of the IPA.

(6)  $\text{N}_2\text{O}_4$ -contaminated Freon 113 can be distilled and recovered after removal of the  $\text{N}_2\text{O}_4$ , by running the contaminated solvent through a caustic-treated celite column.

(7) Trichloroethylene (b. p.  $88^\circ\text{C}$ ) contaminated with hydrocarbon residues can be distilled and the residue treated as Group I oils.

(8) Methyl Ethyl ketone (MEK) (b. p.  $73.4^\circ\text{C}$  as a water azeotrope,  $80^\circ\text{C}$

pure), contaminated with coating residues, can be recovered by distillation and the residue committed to a sanitary landfill.

(9) Mixing of waste substances during the collection and storage operations should be eliminated or reduced to an absolute minimum.

(10) A well-planned system of labeling and accountability is needed for these waste materials.

Our studies in the area have convinced us that the problem of disposal/reclamation of these substances is more involved with proper planning and organization than with technical difficulties or uncertainties. The next steps in preparing for Space Shuttle activities are to establish storage, disposal, and reclamation areas; set up systems and procedures for the collection, labeling, analysis, storage, and treatment of these waste substances; and define new equipment and facilities needs. We believe the magnitude of this job is such as to require one or two professional chemists or chemical engineers, knowledgeable in terms of environmental and toxicological considerations, to thoroughly review all KSC operations that normally generate waste organic materials, and planned Shuttle-related operations, and to prepare final recommendations regarding all aspects of the disposal, reclamation storage, handling, and collection of these materials. The main portion of this effort is projected to be of eighteen to twenty four months duration.

APPENDIX A

REPORT ON THE DISTILLATION OF SOLVENT  
WASTES CURRENTLY STORED AT  
COMPLEX 34, KENNEDY SPACE CENTER

Waste solvents from Complex 34 were tested as part of the Phase 4 study of the disposal of various solvents. These solvents, classified as Group II, had been placed on Complex 34 in 55 gallon drums. Some of these drums had been there for two years or longer. Samples of these solvents were obtained from 27 lots by contractor personnel. Each sample was labelled "Florida Institute of Technology", followed by a digit. Preliminary tests on these solvents were conducted and they are listed as follows:

1. Boiling Point
2. Percent Residue
3. Flash Point
4. Water Solubility

The samples were distilled to determine the boiling points at percentage increments up to a maximum of 300°C. The residue is the material that would not distill at or below 300°C. The flash points were obtained by the open cup method at 22°C and are reported as having a flash point above or below room temperature. The last three columns in the Table denote respectively the contents of the sample according to the label, the contents of the sample according to the test data, and the Florida Institute of Technology recommended disposal method.



# DISTILLATION OF SOLVENT WASTES OBTAINED FROM KSC

NASA No.	Initial B. P. °C of	Boiling Point at End of Percent Distilled										End Point	% Residue	Flash Point	Water Solubility	NASA Contents Claim	F. I. T. Contents Claim	Recommendation
		10%	20%	30%	40%	50%	60%	70%	80%	90%								
F. I. T. #1	232 450	242 468	249 480	254 489	260 500	266 511	276 529	290 554	301 574				20	Above R. T.	None	Hydraulic Oil - Trace of Water	Hydraulic Oil - Trace of Water	Treat as Group I
F. I. T. #2	186 367	193 379	194 381	195 383	196 385	197 387	198 388	199 390	201 394	204 399	206 403	0	Above R. T.	None	None	Contaminated Solvent, Dry Cleaning (FED- SPEC P-D-680) Type 2	Cleaning Solvent	Treat as Group I
F. I. T. #3	70 158	104 219	108 226	121 250	129 264	140 284	153 307	169 336	191 376	220 428	230 446		0	Below R. T.	None	Methanol	Casoline	Reclaim
F. I. T. #4	99 210	100 212	100 212	100 212	100 212	100 212	100 212	100 212	100 212	100 212	100 212			Above R. T.	Soluble	Unknown Drum I. D. DSA-400- 69-0-0205-0003 Geo. Senn, Inc., Phila., Pa.	H <sub>2</sub> O based cleaning solu- tion	Ocean Dump
F. I. T. #5	66 151	139 282	159 318	172 342	184 363	190 374	194 381	197 387	206 403	236 457	252 486	0	Below R. T.	None	None	Paint Stripper- thinner (sampled solvent only - Heavy sediment in bottom not mix- able	"Solvent"	Reclaim
F. I. T. #6	100 212	100 212	100 212	100 212	100 212	100 212	100 212	100 212	100 212	100 212	101 214	0	Above R. T.	Soluble	Soluble	FREON cleaning agent	H <sub>2</sub> O based cleaning solution	Ocean Dump
F. I. T. #7	45 113	45 113	45 113	45 113	45 113	45 113	45 113	45 113	45 113	45 113	52 126	0	Above R. T.	Soluble	Soluble	FREON cleaning agent	FREON cleaning agent	Reclaim
F. I. T. #8	40 104	42 108	45 113	49 120	58 136	222 432	247 477	260 500			260 500	30	Above R. T.	None	None	RP #1 and by- draulic oil	FREON cleaning agent and heavy oil	Reclaim FREON and treat residue as Group I
F. I. T. #9	74 165	100 212	110 230	118 244	124 255	130 266	136 277	148 298			154 309	30	Below R. T.	None	None	Paint Shop Waste	Casoline and 65% H <sub>2</sub> O (upper layer distilled)	Separate and reclaim gasoline. Ocean dump the H <sub>2</sub> O
F. I. T. #10	80 176	210 410	218 424	228 434	240 464	258 496					258 496	50	Above R. T.	None	None	Rust inhibitor per a stick-on label	Used lube oil	Treat as Group I
F. I. T. #11	144 291	200 392									200 392	80	Above R. T.	None	None	"Waste oil"	Used light lube oil	Treat as Group I
F. I. T. #12	78 172	86 187	91 196	94 201	96 205	98 208	99 210	100 212						Above R. T.	Soluble	Water and other	Water and other	Ocean Dump

F.I.T. #13	40 104	49 120	58 136	64 147	76 169	82 180	245 473	298 568	292 558	302 576	10	Above R. T.	None	"Waste oil"	Waste oil and possibly FREON	Reclaim FREON and treat residue as Group I
F.I.T. #14	58 136	99 210	143 289	190 374	254 507	290 554	318 604			Dec.	40	Above R. T.	None	"Thinner/Stripper waste"	"Thinner/Stripper Waste"	Reclaim
F.I.T. #15	48 118	69 156	84 183	90 194	202 396	220 428	228 442	232 450	228 442	210 410	10	Below R. T.	None	Hydraulic oil/ thinner	Thinner	Reclaim thinner, treat residue as Group I
F.I.T. #16	138 280	174 345	177 351	180 356	182 360	183 361	184 363	135 365	186 367	190 374	10	Above R. T.	None	Thinner/hydraulic oil	Kerosene Like	Reclaim
F.I.T. #17	160 320	188 370	190 374	191 376	192 378	193 379	194 381	194 381	194 381	194 381	0	Above R. T.	None	Contaminated P-O-680	Kerosene Like	Reclaim
F.I.T. #18	99 210	99 210	99 210	99 210	99 210	99 210	99 210	102 216	105 223	105 221	0	Above R. T.	Soluble	Waste paint remover	Essentially H <sub>2</sub> O	Ocean Dump
F.I.T. #19	98 208	99 210	99 210	99 210	99 210	100 212	102 216	102 216	102 216	102 216	0	Above R. T.	Soluble	"Waste paint remover"	Contaminated H <sub>2</sub> O	Ocean Dump
F.I.T. #20	42 108	50 122	50 122	50 122	50 122	50 122	50 122	50 122	50 122	50 122		Below R. T.	60% Soluble	No label, may be oil + FREON	Oil, FREON and H <sub>2</sub> O	Separate and: 1) Ocean dump H <sub>2</sub> O layer 2) Reclaim FREON 3) Reclaim oil
F.I.T. #21	72 162	80 176	82 180	85 185	90 194	93 199	98 208	102 216	114 237	116 241	0	Above R. T.	Soluble	Waste J P-5	Waste U.P. 4	Reclaim
F.I.T. #22	120 248	186 367	189 372	191 376	192 378	194 381	195 383	196 385	196 385	198 388	0	Above R. T.	None	Cleaning solvent (plus maybe oils)	Cleaning Solvent	Reclaim
F.I.T. #23	96 205	99 210	102 216	174 345	179 354	180 356	182 360	182 360	188 370	190 374	0	Above R. T.	Soluble	Paint Stripper (phenol odor)	Creosote	Reclaim
F.I.T. #24	120 248	182 360	185 365	186 367	188 367	188 367	189 372	190 374	190 374	191 376	0	Above R. T.	None	Unknown lint sterilized dry cleaning solvent	Cleaning Solvent	Reclaim
F.I.T. #25	98 208	99 210	100 212	176 349	184 363	188 370	190 374	194 381	240 464	270 518	0	Above R. T.	Soluble	Lab oil? How- ever appears too thin	Creosote	Reclaim
F.I.T. #26	79 174	98 208	100 212	100 212	100 212	100 212	100 212	100 212	100 212	100 212	0	Above R. T.	Soluble	Paint stripper/ thinner (four sim- ilar barrels band- ed together)	Essentially H <sub>2</sub> O	Ocean Dump
F.I.T. #27	130 286	174 345	180 356	184 363	185 365	187 368	188 370	190 374	191 376	192 378	0	Above R. T.	None	Dry cleaning solvent XYLENE	Cleaning Solvent	Reclaim

APPENDIX B

COMMUNICATION FROM

STATE OF FLORIDA

DEPARTMENT OF POLLUTION CONTROL

(including a list of Liquid Waste Incinerator Manufacturers)



STATE OF FLORIDA  
DEPARTMENT OF POLLUTION CONTROL

2562 EXECUTIVE CENTER CIRCLE, EAST  
MONTGOMERY BUILDING  
TALLAHASSEE, FLORIDA 32301

PETER P. BALJET  
EXECUTIVE DIRECTOR

January 23, 1975

W.D. FREDERICK, JR.  
CHAIRMAN

Mr. Henry Sivik  
Florida Institute of Technology  
U.C.P.R.  
Country Road  
Melbourne, Florida 32901

Dear Mr. Sivik:

As we discussed during our telephone conversation of January 20th, I am pleased to enclose a list of liquid waste incinerator manufacturers. Also, the Environmental Protection Agency has provided a list of companies in the business of accepting, treating and/or disposing of various hazardous wastes. Two of these companies that we have referred problems of this nature to in the past are:

Rollins Environmental Services, Inc.  
3208 Concord Pike  
Wilmington, Delaware 19899  
Phone: 302/658-8541  
Facilities: Bridgeport, New Jersey; Baton Rouge,  
Louisiana; Houston, Texas  
Materials Handling: liquids and  
slurries only.

Chem-Trol Pollution Services, Inc.  
Post Office Box 200  
Model City, New York 14107  
Phone: 716/754-8231  
Facilities: Landfill and incineration.

Also, in the Southeastern United States are:

Liquid Waste Disposal, Inc.  
Post Office Box 19063  
Louisville, Kentucky 40219

John R. Middlemas  
BOARD MEMBER

Susan Wilson  
BOARD MEMBER

Mark D. Hollis  
BOARD MEMBER

Y.E. Hall  
BOARD MEMBER

Mr. Henry Sivik  
January 23, 1975  
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Phone: 502/968-6173  
Contact: Mr. G. M. O'Bryon  
Facilities: High temperature incineration.  
Materials Handled: Liquids only.

Nuclear Engineering Company, Inc.  
Post Office Box 7246  
Louisville, Kentucky 40207  
Phone: 502/426-7160  
Contact: Mr. Barney Roberts  
Site Locations: Beatty, Nevada; Sheffield, Illinois;  
Robstown, Texas (Texas Ecologists,  
Subsidiary)  
Materials Handled: Liquids, slurries, sludges,  
containers, solids.

It must be noted that these companies are not  
endorsed by EPA nor DPC.

Regarding the incineration of these wastes, the  
permitting and operational information pertaining to  
incinerators is handled on a regional basis; therefore,  
I suggest that you contact any of the following persons  
concerning the acid-scrubbing capabilities of the  
municipal and industrial incinerators in your area.  
They are as follows:

Dave Forehand, Field Operations  
Central Region  
Department of Pollution Control  
Orlando, Florida 32801  
Phone: 305/894-6541

Dave Karsmarski, Regional Air Engineer  
Southeast Region  
Department of Pollution Control  
Fort Lauderdale, Florida 33301  
Phone: 305/524-8593

Joe Tessitore, Regional Air Engineer  
West Central Region  
Department of Pollution Control  
Winter Haven, Florida 33881  
Phone: 813/299-1134

Hans Schmidt  
Dade County Pollution Control  
Phone: 305/635-7524

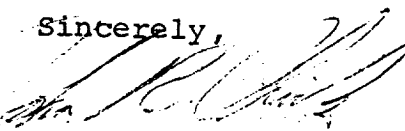
Mr. Henry Sivik  
January 23, 1975  
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Other items of importance are as follows:

1. All chloro-, and chlorofluorohydrocarbons, when heated to decomposition, give off noxious and highly toxic fumes. The fumes consist of the corresponding halo-acids, the free halogens, and in the case of chlorine containing compounds, phosgene.
2. We suggest that you confer with the local air pollution control engineer in the region where you decide to incinerate the wastes, in order to inform him of the case and so that Federal and State guidelines regarding emissions can be met.
3. Due to the explosive nature of ethyl methyl ketone, care should be taken in handling. Empty drums to be disposed of should be "triple-rinsed" and have all openings clear. We have a documented case of an empty ethyl methyl ketone drum (55 gallons), which was closed, being run over in a landfill and exploding, causing the crawler tractor to burn completely. The tractor operator narrowly escaped serious injury.
4. You should confer with your local water pollution control engineers to determine the in-plant measures to reduce the quantities and strength of the wastes being introduced into a municipal sewage treatment plant.
5. By offering this technical assistance, the Department of Pollution Control is not accepting the responsibility for the safe disposal of the wastes herein mentioned.

If we can be of any further assistance, please call. We would greatly appreciate your keeping us informed as to the final disposal of this waste. Thank you.

Sincerely,

  
John R. Chick  
Solid Waste Planning  
Division of Planning

JRC/kc  
Attachments

cc: John A. Redmond

## LIQUID WASTE INCINERATOR MANUFACTURERS

Bartlett - Snow  
6200 Harvard Avenue  
Cleveland, Ohio 44105  
216/883-5700

Besser - Wasteco Corporation  
Roanoke, Illinois 61561  
309/923-2911

Copeland Systems Incorporated  
120 Oakbrook Mall, Suite 220  
Oak Brook, Illinois 60521  
312/654-2820

Environmental Control Products, Inc.  
P.O. Box 15753  
Charlotte, North Carolina 28210  
704/889-7511

Garver - Davis, Inc.  
Pollution Control Systems  
Centerline Building  
19200 Villaview Road  
Cleveland, Ohio 44119  
216/531-0835

North American Manufacturing Co.  
Cleveland, Ohio 44105  
216/271-6000

Peabody Engineering Corporation  
39 Maple Tree Avenue  
Glenbrook, Connecticut 06906

Paneco Manufacturing Co.  
205 West 14 Mile Road  
Royal Oak, Michigan

Ross Engineering  
Machinery Division  
Midland - Ross Corporation  
P.O. Box 751  
New Brunswick, New Jersey 08903  
201/249-1040  
Telex - 844417

Smith Environmental Corporation  
1903 Doreen Avenue  
P.O. Box 3696  
South El Monte, California 91733  
213/686-2155

Thermal Equipment Systems, Inc.  
P.O. Box 2097  
1299 S.W. 13th Street  
Boca Raton, Florida 33432  
305/399-0639  
Representative for:  
Combustion Division  
Eclipse Fuel Engineering Co.  
1100 Buchanan Street  
Rockford, Illinois 61101

Waste Combustion Corporation  
P.O. Box 6295  
Richmond, Virginia 23230

Zurn Industries, Inc.  
Sargent - NCV DID  
610 Devon Street  
Kearny, New Jersey 07032  
201/991-7200

APPENDIX C  
TRIP REPORTS



VISIT TO: Florida Filters, Tampa, Florida

DATE: January 31, 1975

PERSON CONTACTED: Mr. William Souter, Environmental Specialist

PURPOSE: To discuss incinerators, stills, drying and other pollution control equipment.

Florida Filters, in addition to servicing various types of aerosol/particulate filters, also designs pollution control systems, according to Mr. Souter, for air and certain solid wastes. For this purpose Florida Filters uses equipment manufactured by a number of other concerns such as:

Aerosols Control Corp. (mist, fume, etc. air purification equipment)

Comtro, Division of Sunbeam Equipment Corp. (incinerator, etc.)

Interdyne (Solvent Recovery units)

Zurn Industries (Gas Dryers, etc.)

The Comtro incinerator operates at 1500 to 2000<sup>o</sup> F. Though designed for plastic and paper waste disposal, it can be adapted for liquid waste disposal such as combustible solvents by addition of atomizing nozzles, or for halogenated solvents with addition of gas-scrubbing equipment. Basic incinerator cost for a unit capable of handling 100 gallons/hour is about \$9,000, without scrubber.

A unit for solvent recovery (Interdyne Still), with 25 gallons/hour capacity, cost about \$9,000 with operation costs about 3 cents/gallon, all stainless steel construction. This still could be used to recover isopropyl alcohol, freon, or other solvent accumulated in sufficient quantity.

A most interesting discussion was in relation to scrubbers for drying and NO<sub>X</sub> gas removal equipment. Mr. Souter commented on the Zurn Industries equipment utilizing synthetic zeolites to adsorb NO<sub>X</sub> from gaseous

mixtures. He was not aware of its effectiveness but suggested we contact Union Carbide Co., manufacturer of the zeolites. (Union Carbide was contacted by J. Thomas and provided some useful information on their Pura Siv Processes).

Mr. Souter distributed to us manufacturers' descriptive literature from the aforementioned companies. The information gained was worthwhile.

H. Sivik

VISIT TO: SCA Services, Tampa, Florida

DATE: January 31, 1975

PERSON CONTACTED: Mr. Ty Hartley, Director

SCA is a national organization with over 100 operation centers for materials processing, disposal, recovery, and liquid waste treatment (Chem-trol). The Tampa division handles only collection, recovery and disposal of solid wastes, but would collect liquid wastes for processing at their Model City plant.

Mr. Ty Hartley provided some information on his companies' capabilities but not too much technically valuable information to us on solvent disposal or recovery. He asked that samples be submitted for evaluation and quotation of recovery charges. This company provides lab services at \$20 - 22 hour.

H. Sivik

VISIT TO: Honeywell, St. Petersburg, Florida

DATE: January 31, 1975

PERSON CONTACTED: Mr. Bill Huffman

PURPOSE: Discuss incinerators and recovery of liquid wastes.

This was an especially worthwhile visit because of the thorough and interesting presentation by Mr. Huffman and the first hand look at their incinerator.

Honeywell has established a comprehensive program of liquid/solvent classification, disposal and recovery procedure for the waste liquid generated at this location. Part of the motivating force for implementing this program resulted from shortages of certain solvents and part was from safety and EPA requirements.

The incinerator is 30 feet high, propane-fired, having four atomizing nozzles for the combustible liquids, and operates at 1500-1750<sup>o</sup>F. The incinerator is controlled by a semi-automatic control panel and has several built-in safety shut down features. Liquid wastes are combined and stored in a 500 gallon holding tank, prefiltered and then burned as required. Total liquid wastes burned is about 22,000 gallons per year.

A quick breakdown of seven categories of liquid wastes at Honeywell:

1. Waste paper, etc.
2. Combustibles (see list)
3. Acetone - reclaimed
4. Water soluble chemicals - dump to sewer
5. Incombustibles - scavengers paid to dispose of
6. MEK, TRIC, Freon degreasers - recycled
7. IPA recycled due to current shortage

IPA, MEK, freon and other solvents are recycled. Certain incombust-

ibles (low assay trichloroethylene, etc.) are disposed by commercial material handlers.

The wastes are segregated at site of generation by storing in labeled 5-gallon metal safety cans, then collected in a central location for proper disposition/recycling as required by internal specifications.

Two stills are in operation at the present time: one is a 4-6 gallon capacity per 8 hours, the other is a 55 gallon capacity per 8 hours.

According to Mr. Huffman, their waste disposal/recovery system, once implemented, is receiving full cooperation from the numerous sections at this location employing over 1000 people.

VISIT TO: Department of Pollution Control, Orlando, Florida

DATE: February 21, 1975

PEOPLE CONTACTED: Mr. Charles M. Collins and Mr. Tom Hunnicutt

PURPOSE: To discuss disposal methods of liquid wastes

Mr. Collins gave us a brief description of the monitoring work in the solid waste section he is responsible for in the nine counties of central Florida. Mainly, his discussion explained the operation of a hospital incinerator. We also obtained 12 preprints on rules/regulations/pollution information for the state of Florida on air and water pollution.

Little or no worthwhile information was provided on disposal of liquid wastes.

H. Sivik

VISIT TO: City Chemicals, Orlando, Florida

DATE: July 18, 1975

PERSON CONTACTED: Mr. Art Greer, Manager

PURPOSE: To discuss solvent reclamation capabilities of a local firm.

City Chemicals was in the oil supply/reclaiming business for a number of years. Three years ago they increased their scope for solvent reclamation by including aliphatics, aromatics, and chlorinated hydrocarbons, and thinners. Three stills are currently operational with a through-put capability of 1000 gallons per 8 hours or about 2000 gallons per 24 hours. They expect to double this capacity in the car by addition of more stills and a rectifying column. An incinerator is also contemplated. With about 25 employees, annual sales approach \$2 million.

On-site storage capacity is 100,000 gallons including several stainless steel tanks. A 2000 gallon tank wagon and a 7000 gallon transport allows them to pick up and deliver liquids with or without sell-back arrangements.

Mr. Greer has contacted NASA in the past and has expressed interest in solvent reclaiming. Customers include Disney, General Electric, and Westinghouse.

H. Stvik